

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 30-11-2015		2. REPORT TYPE Ph.D. Dissertation		3. DATES COVERED (From - To) -	
4. TITLE AND SUBTITLE Novel Thermoplastic Elastomers based on Benzofulvene: Synthesis and Mechanical Properties			5a. CONTRACT NUMBER W911NF-11-1-0417		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Weiyu Wang			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Tennessee at Knoxville 1534 White Avenue Knoxville, TN 37996 -1529			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 59668-CH.11		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Thermoplastic elastomers (TPEs) are of great importance both academically and technologically. Currently TPEs are the predominant form of styrene-diene copolymers. However, these styrenic TPEs have serious limitations in applications, especially at higher temperature, because of their low upper service temperature (UST). The work described in this dissertation is aimed toward developing thermoplastic elastomers with a higher UST and lower cost. In order to develop TPEs with a higher UST, we employed benzofulvene, an anionically polymerizable					
15. SUBJECT TERMS anionic polymerization, thermoplastic elastomer, phase behavior					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			S. Kilbey
					19b. TELEPHONE NUMBER 865-974-4303

Report Title

Novel Thermoplastic Elastomers based on Benzofulvene: Synthesis and Mechanical Properties

ABSTRACT

Thermoplastic elastomers (TPEs) are of great importance both academically and technologically. Currently TPEs are the predominant form of styrene-diene copolymers. However, these styrenic TPEs have serious limitations in applications, especially at higher temperature, because of their low upper service temperature (UST). The work described in this dissertation is aimed toward developing thermoplastic elastomers with a higher UST and lower cost.

In order to develop TPEs with a higher UST, we employed benzofulvene, an anionically polymerizable monomer in hydrocarbon solvent at room temperature, as the glassy block and copolymerized it with isoprene to prepare polybenzofulvene-polyisoprene-polybenzofulvene (FIF) triblock copolymers. Among all triblock copolymers studied, FIF with 14 vol% of PBF exhibited a maximum stress of 14.3 MPa and strain at break of 1394 % from tensile tests. Dynamic mechanical analysis showed that the upper service temperature of FIF is 145 °C. Microphase separation of FIF triblock copolymers was observed by small angle X-ray scattering, even though long range order was not achieved under the annealing conditions used.

Additionally, we report the effects of partial and complete hydrogenation on the thermal stability, mechanical and morphological properties of high temperature thermoplastic elastomers comprised of polybenzofulvene-polyisoprene-polybenzofulvene (FIF) triblock copolymers. After hydrogenation of polyisoprene and unsaturated carbon bonds in the five member ring of PBF, ultimate tensile stress was reduced to 11.2 MPa with strain at break of 750%. The upper service temperature also decreased to 125 °C. The fully hydrogenated triblock copolymer demonstrated an ultimate stress of 14 MPa at 744 % strain. The glass transition temperature (T_g) of fully hydrogenated PBF was 130 °C. Thermal stability was greatly improved by both partial and complete hydrogenation.

Lastly, we developed a cost efficient method to prepare high molecular weight “comb-shaped” graft copolymers, poly(isoprene-g-styrene), with polyisoprene as the backbone and polystyrene as side chains. The grafted polymers were synthesized via free radical emulsion polymerization by copolymerization of isoprene with a polystyrene macromonomer synthesized using anionic polymerization. A small amount of toluene was used in order to successfully disperse the macromonomer. Both a redox and thermal initiation system were used in the emulsion polymerization. The multigraft copolymers obtained were very high in molecular weight ($5-12 \times 10^5$ g/mol), and up to 10 branches per chain, on average, could be incorporated. A material incorporating 29 wt% polystyrene exhibits a disordered microphase separated morphology and elastomeric properties. These materials show promise as new, highly tunable, and potentially low cost thermoplastic elastomers.

Novel Thermoplastic Elastomers based on Benzofulvene: Synthesis and Mechanical Properties

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Weiyu Wang
December 2015

Copyright © 2015 by Weiyu Wang
All rights reserved.

Acknowledgements

First of all, I gratefully thank my advisor Dr. Jimmy W. Mays for his mentorship which is beyond support, encouragement and guidance throughout my doctoral study throughout pass four and half years. His spirit of collaboration, wisdom of interpersonal skills and passion of career pursuits, constructively influenced my mind-set within and outside graduate school.

I would like to thank my doctoral committee members: Dr. Michael Best for his valuable time and advising, Dr. Michael Kilbey and Dr. Alexei Sokolov for bringing me on board on fascinating fundamental research projects and expanding my knowledge about polymeric materials. I enjoyed and would like to continue our collaboration in my future career.

I sincerely thank Dr. Nam-Goo Kang, Dr. Kunlun Hong (ORNL), Dr. Sang-Woog Ryu (Chungbuk National University, Korea), Dr. Suxiang Deng (GM, China) and Dr. David Uhrig (ORNL) for coaching me with essential experiment techniques when I started in UTK.

Working in Mays' group provided me with various opportunities to interact with world leading polymer scientists and engineers including: Dr. Mario Beiner and Dr. Ralf Schlegel from Fraunhofer institute in German (mechanical properties). Dr. Samuel Gido and Katherine Williams from the University of Massachusetts (TEM and SAXS). Dr. Frank Bates and Yiming Zeng from the University of Minnesota (Parr reactor hydrogenation). Dr. Shi-Qing Wang and Jianning Liu from the University of Akron (rheology).

Additionally, I would also like to thank Dr. Herbert Chao (Total Valley), Dr. Zhiyi Bao (Zeon Chemical), Dr. Naixiong Jin (Eastman) and Ilir Koliqi (Tosoh Bioscience LLC.) for their career advices.

I am also very fortunate to work with professors, post-docs and fellow graduate students in the University of Tennessee and Oak Ridge National Lab including: Dr. Mark Dadmun, Dr. Adam Imel, Dr. Jihua Chen (ORNL) and Halie Martin for TEM. Dr. Yangyang Wang (ORNL), Dr. Shiwang Chen, Dr. Fei Fan, Adam Holt for rheology and dielectric spectroscopy. Dr. Jesse Davis and Kamlesh R. Bornani for light scattering. Dr. Dimitry Voyloy for AFM. Dr. Carlos Steren for NMR. Dr. Chunhui Bao for ATRP and RAFT. Also current and ex- group members in Mays' group including: Dr. Shahinur Rahman, Dr. Kostas Mischronis, Dr. Beomgoo Kang, Tom Malmgren, Dr. Xiaojun Wang, Dr. Justin Roop, Dr. Vikram Srivastava, Dr. Sachin Bobade, Andrew Goodwin, Christopher Hurley, Wei Lu, Xinyi Lu, Hongbo Feng, Benjamin Ripy, Huiqun Wang and Tyler White. It has been a great pleasure to work with all of them. The presence of all these people during my doctoral study are vital for my growth and success. I sincerely appreciate every one of them.

Finally, I would like to thank my father Jimin Wang and my mother Yun Wang for their patience, sacrifice and selfless love which makes today possible. To my grandfather who passed away shortly after I came to Knoxville in 2011, may he rest in peace.

Weiyu Wang

Abstract

Thermoplastic elastomers (TPEs) are of great importance both academically and technologically. Currently TPEs are the predominant form of styrene-diene copolymers. However, these styrenic TPEs have serious limitations in applications, especially at higher temperature, because of their low upper service temperature (UST). The work described in this dissertation is aimed toward developing thermoplastic elastomers with a higher UST and lower cost.

In order to develop TPEs with a higher UST, we employed benzofulvene, an anionically polymerizable monomer in hydrocarbon solvent at room temperature, as the glassy block and copolymerized it with isoprene to prepare polybenzofulvene-polyisoprene-polybenzofulvene (FIF) triblock copolymers. Among all triblock copolymers studied, FIF with 14 vol% of PBF exhibited a maximum stress of 14.3 MPa and strain at break of 1394 % from tensile tests. Dynamic mechanical analysis showed that the upper service temperature of FIF is 145 °C. Microphase separation of FIF triblock copolymers was observed by small angle X-ray scattering, even though long range order was not achieved under the annealing conditions used.

Additionally, we report the effects of partial and complete hydrogenation on the thermal stability, mechanical and morphological properties of high temperature thermoplastic elastomers comprised of polybenzofulvene-polyisoprene-polybenzofulvene (FIF) triblock copolymers. After hydrogenation of polyisoprene and unsaturated carbon bonds in the five member ring of PBF, ultimate tensile stress was reduced to 11.2 MPa with strain at break of 750%. The upper service temperature also decreased to 125 °C. The

fully hydrogenated triblock copolymer demonstrated an ultimate stress of 14 MPa at 744 % strain. The glass transition temperature (T_g) of fully hydrogenated PBF was 130 °C. Thermal stability was greatly improved by both partial and complete hydrogenation.

Lastly, we developed a cost efficient method to prepare high molecular weight “comb-shaped” graft copolymers, poly(isoprene-g-styrene), with polyisoprene as the backbone and polystyrene as side chains. The grafted polymers were synthesized via free radical emulsion polymerization by copolymerization of isoprene with a polystyrene macromonomer synthesized using anionic polymerization. A small amount of toluene was used in order to successfully disperse the macromonomer. Both a redox and thermal initiation system were used in the emulsion polymerization. The multigraft copolymers obtained were very high in molecular weight ($5\text{--}12 \times 10^5$ g/mol), and up to 10 branches per chain, on average, could be incorporated. A material incorporating 29 wt% polystyrene exhibits a disordered microphase separated morphology and elastomeric properties. These materials show promise as new, highly tunable, and potentially low cost thermoplastic elastomers.

Table of Contents

Chapter 1: Recent Advances in Thermoplastic Elastomers based on Synthetic

Polymers.....	20
1.1 Introduction:.....	21
1.2 ABA triblock copolymer type TPEs:	24
1.2.1 Polymers prepared by anionic polymerization	24
1.2.2 Polymers prepared by cationic polymerization.....	34
1.2.3 Polymers prepared by metal catalyzed ring opening polymerization	40
1.2.4 Polymers prepared by controlled radical polymerization techniques	47
1.2.5 Polymers prepared by metathesis polymerization techniques	52
1.3 Star branched polymers for TPEs:	54
1.4 Grafted polymers for TPEs:	59
1.5 Perspective:	70
References:.....	72
Chapter 2: Scope of the Dissertation.....	87
2.1 Research Motivation:	88
2.2 Outline:	90
References:.....	91
Chapter 3: Experimental Techniques	92
3.1 High Vacuum Manifold:	93
3.2 Anionic Polymerization by High Vacuum Techniques:	94
3.3 Synthesizing anionic initiator:	96

References:.....	98
------------------	----

Chapter 4: High Temperature Thermoplastic Elastomers Synthesized by Living

Anionic Polymerization in Hydrocarbon Solvent at Room Temperature..... 99

Abstract:.....	100
----------------	-----

4.1 Introduction:.....	101
------------------------	-----

4.2 Experimental Section:.....	104
--------------------------------	-----

4.2.1 Materials:	104
------------------------	-----

4.2.2 Anionic polymerization of BF monomer:.....	105
--	-----

4.2.3 Anionic polymerization of BF monomer in the presence of additives:	106
--	-----

4.2.4 Diblock copolymerization of BF and isoprene:	106
--	-----

4.2.5 Triblock copolymerization of isoprene and BF:	106
---	-----

4.2.6 Preparation of samples:.....	107
------------------------------------	-----

4.2.7 Measurements:	108
---------------------------	-----

4.3 Results and Discussion:	109
-----------------------------------	-----

4.3.1 Anionic polymerization of BF and glass transition temperature of PBF:.....	109
--	-----

4.3.2 Effects of additives on glass transition temperature:	112
---	-----

4.3.3 NMR analysis of PBF synthesized without additive and with DME as the additive:.....	117
--	-----

4.3.4 Diblock Copolymerization of BF with Isoprene:.....	119
--	-----

4.3.5 Triblock Copolymerization of BF with Isoprene:.....	122
---	-----

4.3.6 Dynamic Mechanical Analysis (DMA):	127
--	-----

4.3.7 Stress-strain behavior of FIF triblock copolymers:	129
--	-----

4.3.8 Microphase separation behavior:	134
4.4 Conclusions:	137
References:	139
Chapter 5: Polybenzofulvene Based Thermoplastic Elastomers: Effects of Partial and Fully Hydrogenation	142
Abstract:	143
5.1 Introduction:	144
5.2 Experimental Section:	147
5.2.1 Materials:	147
5.2.2 Anionic polymerization:	148
5.2.3 Hydrogenation:	150
5.2.4 Preparation of samples:	153
5.2.5 Measurements:	153
5.3 Results and Discussion:	154
5.3.1 Anionic polymerization and complete hydrogenation of homopolybenzofulvene:	154
5.3.2 Anionic polymerization and hydrogenation of polybenzofulvene-b- polyisoprene-b-polybenzofulvene (FIF):	156
5.3.3 Thermal properties:	163
5.3.4 Dynamic mechanical analysis:	163
5.3.6 Atomic force microscopy:	169
5.4 Conclusions:	172

References:.....	172
Chapter 6: Synthesis and Characterization of Graft Copolymers Poly(isoprene-g-styrene) of High Molecular Weight by a Combination of Anionic Polymerization and Emulsion Polymerization.....	176
Abstract:.....	177
6.1 Introduction:.....	178
6.2 Experimental Section:.....	183
6.2.1 Materials:	183
6.2.2 Synthesis of PS macromonomer:.....	184
6.2.3 Synthesis of graft copolymers:.....	184
6.2.4 Characterization:	186
6.3 Results and Discussion	189
6.3.1 Synthesis of PS macromonomer:.....	189
6.3.2 Characterization of latex particles composed of graft copolymers:.....	194
6.3.3 Characterization of “comb” graft copolymers:.....	194
6.3.4 Microphase separation of graft copolymer:	200
6.3.5 Thermal properties of the graft copolymers:	203
6.3.6 Rheological properties of graft copolymers:.....	206
6.4 Conclusions:.....	210
References:.....	211
Chapter 7: Conclusions and Future Perspectives.....	216
7.1 Conclusions:.....	217

7.2. Future Perspectives:	219
7.2.1. Composition Dependence of the Morphology in PBF/PI block copolymers:	219
7.2.2 Effects of additives on the characteristic ratio of PBF:	221
7.2.3: Benzofulvene-Butadiene Rubber:	222
Vita	224

List of Tables

Table 1.1: Mechanical properties of ABA triblock copolymer type TPEs prepared by anionic polymerization in hydrogenation solvent.....	28
Table 1.2: Mechanical properties of ABA triblock copolymer type TPEs prepared by anionic polymerization in polar solvent.....	30
Table 1.3: Mechanical properties of ABA triblock copolymer type TPEs – all acrylic polymers.....	32
Table 1.4: Mechanical properties of ABA triblock copolymer type TPEs based on hydrogenated polymers.....	35
Table 1.5: Mechanical properties of ABA triblock copolymer type TPEs synthesized by cationic polymerization.....	37
Table 1.6: Mechanical properties of ABA triblock copolymer type TPEs – all vinyl ether polymers.....	39
Table 1.7: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ring opening polymerization with PLA as the glassy segment.....	42
Table 1.8: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ring opening polymerization with sustainable resources	44
Table 1.9: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ATRP	49
Table 1.10: Mechanical properties of ABA triblock copolymer type TPEs synthesized by RAFT polymerization	51

Table 1.11: Mechanical properties of ABA triblock copolymer type TPEs synthesized by coordination polymerization	54
Table 1.12: Mechanical properties of star-branched polymer type TPEs synthesized by anionic polymerization.....	57
Table 1.13: Mechanical properties of star-branched polymer type TPEs synthesized by cationic polymerization.....	60
Table 1.14: Mechanical properties of star-branched polymer type TPEs synthesized by ATRP	61
Table 1.15: Mechanical properties of grafted polymer type TPEs synthesized by anionic polymerization	63
Table 1.16: Mechanical properties of grafted polymer type TPEs synthesized by ring opening metathesis polymerization.....	66
Table 1.17: Mechanical properties of grafted polymer type TPEs based on architecture III	69
Table 4.1 Anionic polymerization of BF in benzene in the absence of additives:.....	110
Table 4.2 Anionic Polymerization of BF in benzene in the presence of additives.	115
Table 4.3 Diblock Copolymerization of isoprene and benzofulvene.....	120
Table 4.4 Composition of FIF triblock copolymers.....	124
Table 4.5 Mechanical property parameters of FIF	130
Table 5.1: Anionic polymerization and complete hydrogenation of polybenzofulvene	149
Table 5.2 Anionic polymerization, partial and complete hydrogenation of FIF-14	151
Table 5.3 Mechanical properties of triblock copolymers.....	169

Table 6.1: Recipes for synthesis of PI-g-PS multigraft copolymers.....	185
Table 6.2 Average molecular weights and compositions of macromonomer and multigraft copolymers as measured by SEC and ^1H -NMR.	198
Table 7.1 Mechanical properties of PBF based TPEs.....	218

List of Schemes

Scheme 4.1 DLI approach to synthesize FIF triblock copolymer	123
Scheme 5.1 Partial hydrogenation of FIF-14	152
Scheme 5.2 Complete hydrogenation of FIF-14	152
Scheme 6.1: Emulsion copolymerization strategy for obtaining graft copolymer by macromonomer method.	182
Scheme 6.2: The synthetic route to PS macromonomer. (a) the synthesis procedure for hydroxyl-terminated PS; (b) Steglich esterification reaction for synthesis of PS macromonomer.	184
Scheme 6.3 The synthetic route to poly(isoprene-g-styrene) multigraft copolymer via free radical emulsion copolymerization.	187

List of Figures

Figure 1.1: a) Applications of SBCs. b) Global Market of SBCs.....	23
Figure 1.2: Schematic of SIS TPEs.	26
Figure 1.3: CO ₂ separation plots for poly(6-acetoxyhexyl vinyl ether) and poly (2-(2-methoxyethoxy)ethyl vinyl ether) based triblock copolymers together with commodity polymers [polystyrene, natural rubber, and poly(vinyl chloride)] for comparison.....	41
Figure 1.4: (A) Total biosynthetic pathway for the production of MVL. (B) A semisynthetic route to produce MVL from mevalonate. (C) Conversion of MVL to an elastomeric triblock polymer that can be repeatedly stretched to 18 times its original length without breaking.	45
Figure 1.5: Illustration of a Zn ²⁺ /VHV hybrid via metal-ligand complexation.....	48
Figure 1.6: Triblock TPEs based on PMCH and a-PP.....	53
Figure 1.7: S(IS') ₃ miktoarm star copolymer type TPEs.....	58
Figure 1.8: a). Illustration of multigrafted copolymers based on PI backbone and PS branches. b). Chain conformation of multigrafted copolymers in microphase-separated state	64
Figure 1.9: Illustration of TPEs' architecture	67
Figure 1.10: Design concept and synthesis of nanostructured elastomers mimicking the mechanical properties of human skin. (a) ATRP macroinitiator, (b) Cross-linked brush polymers were synthesized and self-assembled into two-phase morphology. (c) Two phase	

morphology of CBPs can be reconfigured into that close to the skin microstructure model.

.....	68
Figure 3.1: High vacuum manifold.....	93
Figure 3.2: Glass apparatus for anionic polymerization of styrene	94
Figure 3.3: Distill benzene in anionic polymerization apparatus	95
Figure 3.4: Final reactor for anionic polymerization.....	96
Figure 3.5: Glass apparatus to prepare <i>sec</i> -BuLi	97
Figure 4.1 SEC curve of PBF synthesized in benzene at room temperature with <i>sec</i> -BuLi. (Denote: PBF is polybenzofulvene and R1 to R7 is run 1 to run 7 in Table 4.1).....	111
Figure 4.2 Additives for anionic polymerization of BF in benzene: (a) DME, (b) DABCO, (c) TMEDA, and (d) <i>sec</i> -BuOLi for anionic polymerization of BF	114
Figure 4.3 T_g versus M_n of PBF synthesized with different additives: DME (red cycle), <i>sec</i> -BuOLi (blue triangle), TMEDA (pink triangle), DABCO (green square) and no additives (black square).	116
Figure 4.4 Possible dimers of PBF.....	117
Figure 4.5 ^{13}C -NMR of PBF: a) ^{13}C -NMR of PBF-10, b) DEPT of PBF-10, c) ^{13}C -NMR of PBF-DME-16, d) DEPT of PBF-DME-16	118
Figure 4.6 SEC curve of PI and PI- <i>b</i> -PBF diblock copolymer.....	121
Figure 4.7 SEC curve of FIF triblock copolymers.....	125
Figure 4.8 ^1H -NMR of FIF-22 measured in THF- d_8	126
Figure 4.9 DMA of FIF triblock copolymers: (a) Storage Modulus vs. Temp. and (b) Loss Modulus vs. Temp.	128

Figure 4.10 Stress-strain curve of FIF triblock copolymers	131
Figure 4.11 Non-affine tube model analysis of FIF triblock copolymers.....	133
Figure 4.12 SAXS data for FIF triblock copolymers.....	135
Figure 4.13 DSC measurement of FIF triblock copolymers, PBF-20 and polyisoprene homopolymers.....	136
Figure 4.14 AFM of FIF-10: a-1) topology, a-2) phase contrast, a-3) force modulation and FIF-14: b-1) topology, b-2) phase contrast, b-3) force modulation.....	138
Figure 5.1: GPC of complete hydrogenation of a) PBF-12 and b) PBF-DME.....	155
Figure 5.2 NMR of complete hydrogenation of PBF-12	157
Figure 5.3: TGA of complete hydrogenation of PBF-12.....	158
Figure 5.4 DSC of complete hydrogenation of a) PBF-12 and b) PBF-DME	159
Figure 5.5 ¹ H-NMR of partial and complete hydrogenation of FIF-14	161
Figure 5.6: GPC of partial and complete hydrogenation of FIF-14.....	162
Figure 5.7 TGA of partial and complete hydrogenation of FIF-14	164
Figure 5.8 DSC of partial and complete hydrogenation of FIF-14.....	165
Figure 5.9 DMA of a) FIF-14 and b) FH-FIF-14.....	167
Figure 5.10: Tensile test of FIF-20 and PH-FIF-20.....	168
Figure 5.11: Tensile test of FH-FIF-20.....	170
Figure 5.12: AFM of a) Height Image of FIF-14, b) Phase Image of FIF-14, c) Height Image of FH-FIF-14, d) Phase Image of FH-FIF-14.....	171
Figure 6.1 SEC chromatogram for polystyrene macromonomer.....	191
Figure 6.2 ¹ H-NMR spectrum of polystyrene macromonomer.....	192

Figure 6.3 MALDI-TOF mass spectrum of PS macromonomer.	193
Figure 6.4 DLS size results for latex particles formed by graft copolymerization of macromonomer and isoprene, (a) for sample MG-3-3; (b) for sample MG-3-5.	195
Figure 6.5. SEC chromatograms for PS macromonomer and multigraft copolymers before and after fractionation.	196
Figure 6.6 a) The chain structure and ^1H -NMR spectrum of MG-3-3 dissolved in CDCl_3 ; b) ^{13}C -NMR spectrum of MG-3-3 dissolved in CDCl_3	199
Figure 6.7: AFM phase image of MG-3-5 over an area of $2\ \mu\text{m} \times 2\ \mu\text{m}$	201
Figure 6.8: TEM image of MG-3-5	202
Figure 6.9: TGA thermograms for poly(isoprene-g-styrene) multigraft copolymers....	204
Figure 6.10: DSC thermograms for PI homopolymer, MG-3-3, MG-3-5, and PS macromonomer.	205
Figure 6.11: Storage modulus G' (solid symbols) and loss modulus G'' (hollow symbols) for MG-3-3 (■, □) and MG-3-5 (▲, △) as a function of frequency.....	208
Figure 6.12: Tan δ versus frequency for MG-3-3 and MG-3-5.....	209
Figure 7.1: Proposed research on composition dependence of the morphology in PBF/PI block copolymers	220
Figure 7.2: Proposed Study of Effects of Additives on PBF	221
Figure 7.3: Benzofulvene-Butadiene Rubber	Error! Bookmark not defined.

Chapter 1: Recent Advances in Thermoplastic Elastomers based on Synthetic Polymers

1.1 Introduction:

Thermoplastic elastomers (TPEs) are biphasic synthetic polymer materials consisting of a continuous soft rubbery matrix physically cross linked by glassy plastic domains.^{1,2} Such materials have the elasticity of conventional rubber but are suitable for high throughput plastic processing techniques such as injection molding and melt extrusion without requiring a curing process.^{3,4} This feature allows TPEs to be manufactured on a large scale using short production times, which makes TPEs one of the most commonly used polymeric materials in many fields.⁵

Based on chemical composition and morphology, commercially available TPEs can be categorized into six different groups:³ (1) thermoplastic polyurethanes (TPUs), (2) styrenic thermoplastic elastomers (S-TPEs), (3) rubbery-polyolefin blends (TPOs), (4) thermoplastic vulcanizates (TPVs), (5) copolyesters thermoplastic elastomers (TPC-ET) and (6) thermoplastic polyamides (TPA). These have been extensively reviewed in many handbooks.⁴⁻⁷

As a brief historical introduction of thermoplastic elastomers, polyurethanes fibers started to emerge in the plastic/rubber market in the early 1950s with the discovery and development of basic diisocyanate addition.⁸ In 1952, Snyder first patented multiblock linear copolyester fibers with stress and strain characteristics competitive with nature rubber. From the current point of view, these materials would be considered as multiblock TPUs.⁹ Many other polyurethane based thermoplastic gum elastomers were introduced by Bayer, Dupont and Goodyear in late 1950s.¹⁰

Polyurethane based TPEs showing high abrasion resistance with excellent elasticity and tensile strength were commercialized by B.F Goodrich in 1960s.¹¹

A significant event in the development of TPEs was in 1965, when Milkovich and Holden from Shell Development Company synthesized and characterized ABA triblock copolymers based on polystyrene as the hard segment (A block) and polyisoprene as the rubbery matrix (B block) by living anionic polymerization.¹² The termination free (living) anionic polymerization technique allowed styrenic TPEs to be prepared with predicted molecular weight, narrow molecular weight distribution and quantitative yield with negligible impurities in a short production cycle.¹³ The stress-strain and elongation recovery of styrenic TPEs displayed similar behavior to conventional vulcanized rubber without filler reinforcement or crosslinking.¹⁴ This new type of TPE with lower cost and well-defined structure, along with living anionic polymerization,^{15,16} stimulated numerous research activities in polymer thermodynamics,¹⁷ self-consistent field theory¹⁸ and polymer solution properties¹⁹ for the interest of both academic research and industrial applications.

Shell Chemical quickly realized the potential of processing styrenic TPEs (later given the trade name Kraton[®]) with injection molding and melt extrusion. After almost 50 years, styrenic block copolymers (SBCs) have developed into one of the major products in the field of plastic/elastomer industry, and they are used in many fields such as paving, roofing, footwear, coatings, adhesives, sealants, medical tubing and some other advanced systems.²⁰ The global consumption of styrenic block copolymers,

meanwhile, was predicted to increase from 1.8 million tons (5.5 billion US dollars) in 2013 to 2.5 million tons (8.4 billion US dollars) in 2020 with an annual growth rate of 4.5% (**Figure 1.1**).²¹

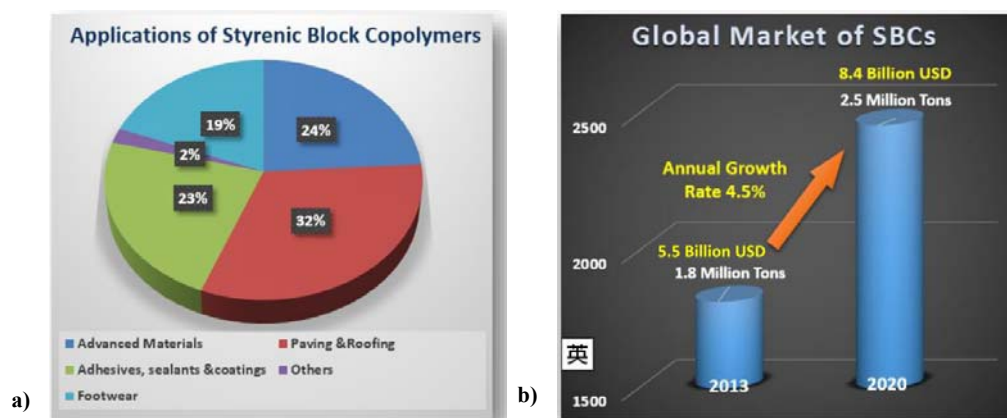


Figure 1.1: a) Applications of SBCs. b) Global Market of SBCs.²¹

Many other types of TPEs were introduced from the 1960s to 1980s. Hercules Inc. in 1966 patented the first thermoplastic polyolefin blends (TPO) based on mixtures of elastic poly(ethylene-co-propylene) (PEP) with over 50% of crystalline polypropylene (PP).²² In late 1970s, Monsanto Company started to focus on a dynamic vulcanization process to chemically crosslink blends of PEP-diene and PP, which was commercialized with trade name of Santoprene® (TPV).²³ Copolyester thermoplastic elastomers (TPC-ET) named Hytrel®, commercialized by DuPont in 1972, combined good mechanical properties with chemical and heat resistance.⁵ Dow Chemical Company developed Estamid® in 1982, a segmented polyamide based thermoplastic elastomer (TPA) with low density, superior mechanical properties at low temperature (-40°C) and service temperature above 200°C.⁸

Starting from the 1990s, many companies strategized their TPE research focus on specific market applications by adding new monomers, functionalities and using sustainable resources to improve properties of existing TPEs systems. In scientific research communities, fascinating polymers with various functionalities, well-defined structures and advanced macromolecular architectures were prepared thanks to developments in living/controlled polymerization techniques such as living anionic^{16,24}/cationic polymerization,²⁵ atomic transfer radical polymerization (ATRP),²⁶ ring opening metathesis polymerization (ROMP),²⁷ reversible addition-fragmentation chain transfer polymerization (RAFT),²⁸ nitroxide mediated radical polymerization (NMRP)²⁹ and so on. However, a large gap still exists between reactions on a laboratory scale and synthesis at the scale of pilot plants. Along with innovations in synthetic polymer chemistry, this chapter summarizes recent advances in thermoplastic elastomers based on synthetic polymers from the aspect of polymer architectures including: (1) ABA type triblock polymers, (2) grafted polymers and (3) star branched polymers. Service temperature, tensile properties of stress and strain at break will be summarized for different composition and architectures. The difference between TPE research in academia and industry will be addressed as the perspective.

1.2 ABA triblock copolymer type TPEs:

1.2.1 Polymers prepared by anionic polymerization:

The most common ABA triblock copolymers type TPEs are polystyrene-b-polyisoprene-b-polystyrene (SIS) and polystyrene-b-polybutadiene-b-polystyrene

(SBS) triblock copolymers. Three things need to be taken into consideration when designing the composition of SIS type triblock copolymers for TPEs applications: (1) Under the designed composition, PI needs to form a continuous rubbery matrix to provide enough elasticity. (2) Overall molecular weight needs to be high enough to drive micro-phase separation for efficient stress reinforcement. (3) Molecular weight should also not be too high considering that high viscosity may cause difficulty in processing and achieving ordered phase separation in the melt.³⁰

In a typical SIS TPE, the molecular weight (M_n) of PS is generally targeted at 10 to 15 kg/mol whereas the M_n of PI is targeted at 50 to 70 kg/mol.³¹ Due to the thermodynamic incompatibility between PS and PI, the minor component PS will micro-phase separate from PI, forming either spherical (less than 20 vol% PS) or cylindrical (20 vol% to 35 vol% of PS) glassy domains, which act as physical crosslinks and reinforce the entangled PI rubbery matrix (**Figure 1.2**). In a dynamic mechanical analysis of SIS with temperature ramp/frequency sweep, SIS behaves like a glassy plastic with a high storage modulus (G') when the temperature is below the glass transition temperature of PI ($T_g \sim -56^\circ\text{C}$). As the temperature increases but remains lower than the T_g of PS (95°C), the polyisoprene chains start to move and G' reaches the rubbery plateau value. This temperature range is considered as the service temperature range where such polymers act as elastomer with typical stress-strain behavior. When the temperature is above 95°C , the polymer enters the melt flow zone and behaves as a viscous liquid. Most TPEs are processed by melt extrusion or injection

molding with processing temperature higher than T_g or melting temperature (T_m) where elastic and glassy domains are miscible and the system is in one phase.

As many applications benefit from low cost S-TPEs, high temperature applications and other advanced consumptions of S-TPEs, such as in tire rubber, are largely limited by the relative low glass transition temperature of PS. When the service conditions approach 95 °C, softening of PS domains dramatically reduces the tensile stress of S-TPEs. One major research interest in the field of anionic polymerization is to increase the upper service temperature of S-TPEs without changing the polymerization procedure, which has already existed in pilot plants for almost 50 years.¹⁴

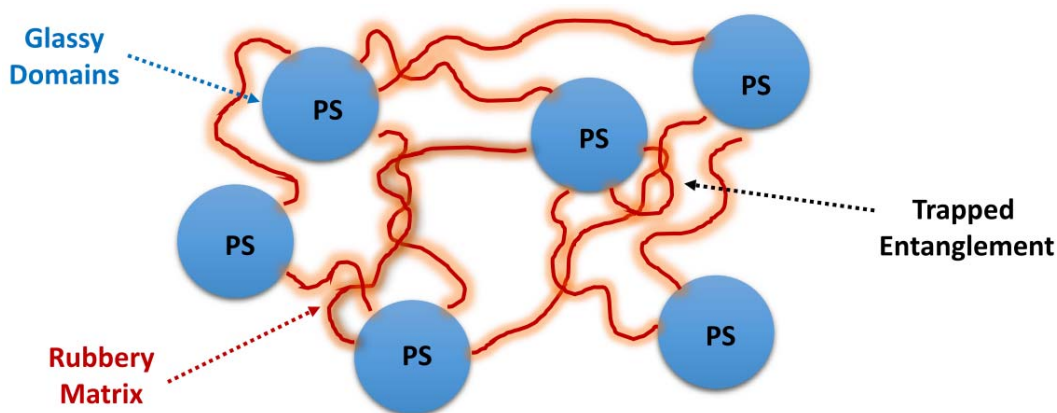
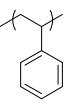
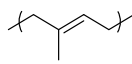
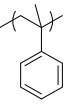
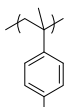
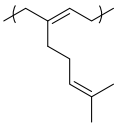
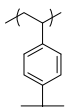
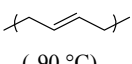
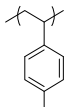
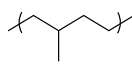
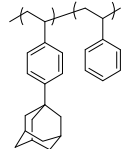
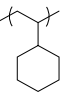
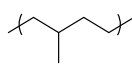


Figure 1.2: Schematic of SIS TPEs.

Many strategies and alternative monomers have been explored by using anionic polymerization in order to improve the upper service temperature (UST) of TPEs. The first strategy was to use *styrene derivatives* with functionalities at α - or *para*- position such as poly(α -methyl styrene) ($T_g \sim 173$ °C),³² poly(α -methyl *p*-methyl styrene) (T_g

~183 °C),³³ poly(*tert*-butyl styrene) (PtBS, T_g ~130 °C)³⁴ and poly(*p*-adamantyl styrene) (P-AdmS, T_g ~ 203 °C).^{35,36} In order to achieve quantitative yield, anionic polymerization of α -methyl styrene generally requires low polymerization temperature (-78 °C) in polar solvent (THF) due to the low monomer ceiling temperature caused by the bulky methyl group at the α position.³² High T_g polystyrene derivatives with bulky pendent groups such as *tert*-butyl or adamantyl, at the *para* position will cause phase blending with polydienes due to the lipophilic nature of the *tert*-butyl or adamantyl group. In order to increase the strength of phase separation and generate effective physical crosslinking, high overall molecular weight is required for polybutadiene/poly(*tert*-butyl styrene) (PtBS, T_g ~130 °C) systems³⁴. Another approach to increase stress was through catalytic hydrogenation of polydienes into polyolefin, which was used in designing TPEs based on polyisoprene and poly(*p*-adamantyl styrene).³⁶ Catalytic hydrogenation to fully saturate PS, forming poly(vinylcyclohexane) (PVCH, T_g ~147 °C), produced TPEs with higher UST and better thermal stabilities.^{37,38} Mechanical properties and service temperatures of all the above mentioned TPEs are summarized in **Table 1.1**, no 1-5.

Table 1.1: Mechanical properties of ABA triblock copolymer type TPEs prepared by anionic polymerization in hydrogenation solvent


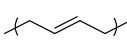

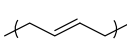



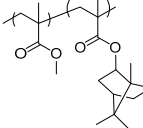
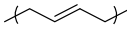
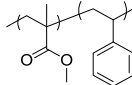
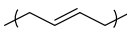
No.	Hard Segment (T_g , °C)	Soft Segment (T_g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
1	 (95 °C)	 (-64 °C)	25.5MPa	1200%	33%	Anionic PLZ (THF, -78 °C)	32
	 (173 °C)		44.6MPa	1100%	33%		
2	 (182 °C)	 (-39 °C)	0.5 to 10.8 MPa	525% to 1340%		Anionic PLZ (THF, -78 °C) Coupling Reaction	33
3	 (130 °C)	 (-90 °C)	24.6 MPa	1080%	50%	Anionic PLZ (benzene, r.t.)	34
4	 (180 °C)	 (-60 °C)	22.3 MPa	590%	45%	Anionic PLZ (CH _x , 40 °C) Catalytic Hydrogenation	35
	 Ran. Copolymer (150 °C)		23.9 MPa	660%	25%		
5	 (147 °C)	 (-60 °C)	28 MPa	652%	39.5%	Anionic PLZ (CH _x , 40 °C) Catalytic Hydrogenation	38

A second anionic polymerization strategy to improve UST was to use methyl methacrylate and its derivatives as the hard segment with polybutadienes (PB) or poly(n-butyl acrylate) (PnBA) as the soft segment.

Since the glass transition temperature of poly(alkyl methacrylate) depends both on tacticity and size of alkyl substituents,^{39,40} incorporating methacrylate derivatives with different tacticities as the hard segment in ABA type triblock copolymers could tune the service condition over a large temperature range.⁴¹ When using polydienes as the elastic matrix, methacrylate derivatives were initiated in THF at -78 °C through a difunctional polydiene anion, which was synthesized in a hydrocarbon solvent since anionic polymerization of butadiene or isoprene in polar solvents forms less cis-1,4 microstructure, and thus dramatically increased the T_g .^{42,43} Methyl methacrylate polymerized by this method contains 75 to 79 % of syndiotactic repeating units and has a glass transition temperature higher than 120 °C³⁹ (**Table 1.2**, no. 6).

Other methacrylate derivatives, such as poly(ethyl methacrylate) (PEMA, $T_g \sim 90^\circ\text{C}$), poly(tert-butyl methacrylate) (PtBMA, $T_g \sim 116^\circ\text{C}$) and poly(isobornyl methacrylate) (PIBMA, $T_g \sim 202^\circ\text{C}$), also could be anionic polymerized by similar methods⁴⁰. Resulting triblock copolymers with polybutadiene as the rubbery matrix displayed high ultimate stress at break and strain at break over 500 %. Notice that when PIBMA was used as the rigid block, triblock copolymers exhibited 600 % strain at break with ultimate tensile stress of 2.2 MPa even when the temperature was 150 °C.⁴¹ Tuning UST from 130 °C to 149 °C was possible by randomly copolymerizing









Table 1.2: Mechanical properties of ABA triblock copolymer type TPEs prepared by anionic polymerization in polar solvent

No	Hard Segment (T _g , °C)	Soft Segment (T _g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
6	 (120 °C)	 (-62 °C)	34.0 MPa	890%	36%	Anionic PLZ (CHx/ether, 25 °C) Anionic PLZ (CHx/THF, -78 °C)	39,4 2
7	 (90 °C)	 (-60 °C)	18.7 MPa	1120%	35%	Anionic PLZ (CHx/ether, 25 °C) Anionic PLZ (CHx/THF, -78 °C)	40,4 1
	 (116 °C)		24.4 MPa	1080%	29%		
	 (132 °C)		32.0 MPa	835%	38%		
	 (160 °C)		35.0 MPa	650%	42%		
8	 Ran. Copolymer (130 - 149 °C)	 (-58 °C)	24.0 MPa	1000%	34%	Anionic PLZ (CHx/ether, 25 °C)	44
			27.0 MPa	1000%	31%	Anionic PLZ (CHx/THF, -78 °C)	
			30.0 MPa	1100%	24%	Anionic PLZ (CHx/THF, -78 °C)	
9	 Block Copolymer (118 °C)	 (-60 °C)	32.0 MPa	900%	13% (PMMA) 25% (PS)	Anionic PLZ (CHx/ether, 25 °C) Anionic PLZ (CHx/THF, -78 °C)	45,4 6

IBMA with MMA with different feed ratios.⁴⁴ UST of styrenic TPEs were enhanced by incorporating MMA as the minor component (13 wt%) in linear PMMA-PS-PB-PS-PMMA pentablock terpolymers TPEs (32 MPa ultimate stress, 900 % strain at break)^{45,46} (**Table 1.2**, no. 7-9).

The above mentioned TPEs systems contained polybutadiene as the elastic block. In all acrylic TPEs where poly(alkyl acrylate) was used as the soft block, TPEs have better UV and oxidation resistance due to the lack of unsaturation.⁴⁷⁻⁵⁵ A typical all acrylic TPE, PMMA-PnBA-PMMA triblock copolymers, was prepared by transalcoholysis of PMMA-poly(tert-butyl acrylate)-PMMA precursor which was synthesized by sequential anionic polymerization of MMA, tert-butyl acrylate and MMA in THF at -78 °C.^{47,48} By keeping the molecular weight of PnBA at 100 kg/mol and varying the weight percentage of PMMA from 9.1 % to 50 %, the ultimate tensile strength was increased from 1.8 MPa to 16.1 MPa where the elongation at break decreased from 1016 % to 228 %.⁴⁸ (**Table 1.3**, no. 10) Difunctional atom transfer radical polymerization (ATRP) initiator was employed to prepare PMMA-PnBA-PMMA triblock copolymers without transalcoholysis.⁴⁹ Tong compared mechanical properties of two different PMMA-PnBA-PMMA triblock copolymers synthesized by anionic polymerization and ATRP with similar molecular weight and composition. The sample prepared by anionic polymerization showed much higher initial stress, modulus with ultimate stress of 8.6 MPa and strain at break of 700 %. The sample prepared by

Table 1.3: Mechanical properties of ABA triblock copolymer type TPEs – all acrylic polymers

No.	Hard Segment (T _g , °C)	Soft Segment (T _g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
10	 (126 °C)	 (-40 °C)	1.8 MPa	1016%	9.1%	Anionic PLZ (THF, -78 °C) Transalcoholysis (PTSA, 150 °C)	48
			14.7 MPa	610%	28.6%		
			16.1 MPa	228%	50.0%		
11	 (107 °C)	 (-40 °C)	8.6MPa	700%	24.2%	Anionic PLZ (THF, -78 °C) Transalcoholysis (PTSA, 150 °C)	50
12	 (117 °C)	 (-21 °C)	7.1MPa	480%	22.2%	Anionic PLZ (THF, -78 °C) Transalcoholysis (PTSA, 150 °C)	54,55
		 (-35 °C)	15.2MPa	680%	21.1%		
		 (-50 °C)	16.4MPa	390%	22.8%		

ATRP, however, broke at 400 % of strain with ultimate stress of 4.1 MPa⁵⁰ (**Table 1.3**, no. 11). The reason will be discussed later in **section 1.2.4**.

The mechanical properties of all acrylic TPEs are generally inferior to styrenic TPEs due to phase blending and high entanglement molecular weight (M_e) of poly(alkyl acrylate) (M_e for PB is 1,700 g/mol whereas M_e for PnBA is 28,000 g/mol).⁵¹ Longer alkyl substitution enhanced the strength of phase separation with PMMA but also increased the M_e and decreased strain at break. The glass transition temperature decreased as the length of alkyl substitution increased.^{52,53} By using different alcohols during transesterification, all acrylic TPEs with poly(ethyl acrylate), poly(n-propyl acrylate) and poly(iso-octyl acrylate) as the elastic middle block were synthesized.⁵⁴ With similar composition (22 wt% of PMMA) and overall molecular weight, all acrylic TPEs with poly(iso-octyl acrylate) as the middle block showed the highest ultimate stress (16.2 MPa) but lowest strain at break (390 %) compared to TPEs with other middle blocks.⁵⁵ (**Table 1.3**, no. 12)

A third anionic polymerization strategy to improve UST is to use *rigid conjugated diene monomers* such as 1,3-cyclohexadiene (CHD) as the glassy block. One feature of anionic polymerization of conjugated dienes is that the microstructure of the resulting polymer varies with different initiation systems. 1,3-cyclohexadiene demonstrated controlled anionic polymerization behavior with three different initiation systems: n-BuLi/tetramethylethylenediamine (TMEDA), n-BuLi/1,2-dimethoxyethane (DME), or sec-BuLi/1,4-diazabicyclo[2.2.2]-octane (DABCO).^{56,57} Resulting poly(1,3-

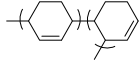
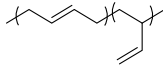
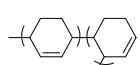
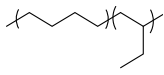
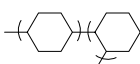
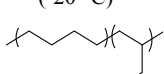
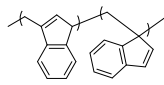
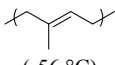
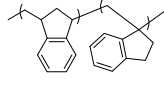
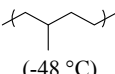
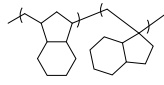
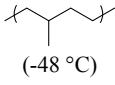
cyclohexadiene) (PCHD) has 55 %, 75 % and 90 % of 1,4-addition respectively. T_g of these polymers decreased from 155 °C to 110 °C as the percentage of 1,2-microstructure was decreased. PCHD-PB-PCHD⁵⁸ triblock copolymer with 30 wt% of PCHD exhibited 10.2 MPa ultimate stress with a relatively low strain at break of 290 %. This might be due to side reactions during anionic polymerization of CHD. By partial hydrogenation of PB without saturated PCHD, ultimate stress increased to 14.0 MPa with better strain at break of 570 %, which indicated a stronger physical crosslinking. The end block PCHD of this triblock copolymer was completely hydrogenated into polycyclohexane, a polyolefin with T_g above 231 °C.⁵⁹ The completely hydrogenated triblock copolymers displayed 10.0 MPa tensile stress at 600 % strain without breaking. (Table 1.4, no. 13)

1.2.2 Polymers prepared by cationic polymerization:

The late 1960s witnessed the rapid development of styrenic thermoplastic elastomers from research in laboratories to commercial products. S-TPEs suffered from two major disadvantages: (1) The upper service temperature limited many advanced applications of S-TPEs. (2) Polydiene middle block's lack of tolerance to strong UV and oxidation. Hydrogenation to saturate polydienes improves the resistance of S-TPEs to UV. However, tertiary protons introduced after hydrogenation lacked stability to strong oxidation reagents.⁶⁴

A renaissance in living cationic polymerization²⁵ advanced many research towards TPEs with better UV/oxidation stability and higher UST. Many cationically-





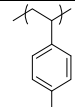

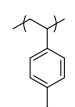
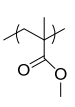
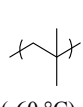
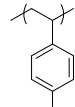

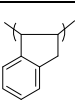
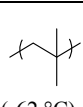
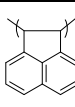
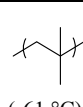
Table 1.4: Mechanical properties of ABA triblock copolymer type TPEs based on hydrogenated polymers

No	Hard Segment (T_g , °C)	Soft Segment (T_g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
13	 (140 °C)	 (-60 °C)	10.2 MPa	290%	30 %	Anionic PLZ (CHx, 40 °C) Catalytic Hydrogenation	58
	 (140 °C)	 (-20 °C)	14.0MPa	570%	30%		
	 (200 °C)	 (-20 °C)	10.8MPa>	600%>	30%		
14	 (145 °C)	 (-56 °C)	14.3 MPa	1390%	20%	Anionic PLZ (benzene, r.t.) Catalytic Hydrogenation	62, 63
	 (125 °C)	 (-48 °C)	11.2 MPa	750%	20%		
	 (135 °C)	 (-48 °C)	16.8 MPa>	510%>	20%		

synthesized TPEs used polyisobutylene (PIB) as the elastic middle block due to its softness and chemical resistance. Triblock copolymer PS-PIB-PS prepared by sequential living cationic polymerization through a difunctional initiator displayed an ultimate tensile stress of 26 MPa, which was competitive with commercial Kraton SIS TPEs.^{65,66} The molecular weight of PIB should targeted between 40,000 to 160,000 g/mol in order to promote tensile properties. Phase separation was observed between PS and PIB when the M_n of PS was above 5000 g/mol. Other triblock copolymers with PIB as the elastic middle block and glassy end block of polystyrene derivatives, such as poly(α -methyl styrene),^{67,68,69,70} poly(*p*-methyl styrene)⁷¹ and poly(*tert*-butyl styrene),⁶⁹ were also synthesized by living cationic polymerization. PMMA-PIB-PMMA triblock copolymer was prepared by a cationic/anionic mechanism switching process.⁷² All these triblock copolymers demonstrated similar stress-strain behavior compared to TPEs developed by anionic polymerization with polydienes as the rubbery matrix. (**Table 1.5**, no. 15-18)

One feature that distinguishes cationic polymerization from anionic polymerization is the ability to control the polymerization of high T_g monomers such as *p*-chlorostyrene (*p*CS),⁷¹ indene (ID)^{69,73} and acenaphthylene (ACP).⁷⁴ Triblock copolymers using *p*CS (T_g , 129 °C), PID (T_g , 225°C) or PACP (T_g , 250°C) as the hard segment and PIB as the soft segment were successfully prepared by cationic polymerization and showed stress-strain behavior similar to typical TPEs. Notice that

Table 1.5: Mechanical properties of ABA triblock copolymer type TPEs synthesized by cationic polymerization



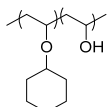

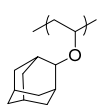
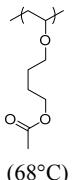
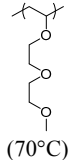
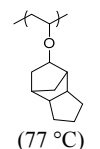
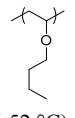
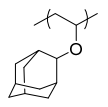

No.	Hard Segment (T_g , °C)	Soft Segment (T_g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
15	 (89 °C)	 (-61 °C)	26MPa	760%	25.1%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C)	65
16	 (180°C)	 (-61 °C)	24.5MPa	370%	44.7%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C)	70
			11.5MPa	830%	22%		
17	 (110 °C)	 (-62 °C)	15.1MPa	560%	32%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C)	71
	 (130 °C)		18.1MPa	400%	50%		
18	 (108 °C)	 (-60 °C)	14.5MPa	650%	34%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C) Anionic PLZ (CHx, 40 °C)	72
19	 (123 °C)	 (-61 °C)	21MPa	460%	38%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C)	71
			10MPa	1200%	30%		
20	 (225 °C)	 (-62 °C)	15.7MPa	600%	20.5%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C)	73
			20.5MPa	400%	40%		
21	 (250 °C)	 (-61 °C)	14.7MPa	793%	13%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C)	74

PpCS is a polar polymer with weather and flame resistance. Indene is potentially a very cost effective monomer for high temperature applications. (**Table 1.5**, no. 19-21)

Alkyl vinyl ethers are another unique group of monomers polymerized by living cationic polymerization. Hydrolysis of cationically synthesized poly(tert-butyl vinyl ether) (PtBVE) produced well defined poly(vinyl alcohol) (PVA).⁷⁵ As a widely used water soluble polymer in coating and textiles, semicrystalline PVA has a T_g of 80 °C and T_m of 208 °C which makes it a candidate for TPEs with oil resistance. PVA-PIB-PVA triblock copolymer could be prepared by direct hydrolysis of PtBVE-PIB-PtBVE. However, mechanical properties were not measured since the resulting polymers had very limited solubility and were largely degraded by thermal processing. Cyclohexyl vinyl ether (CHVE) could be statistically copolymerized with tert-butyl vinyl ether by living cationic polymerization initiated from difunctional polyisobutylene living cation. Hydrolysis of the resulting triblock copolymers yielded P(CHVE-stat-VA)-PIB-P(CHVE-stat-VA)⁷⁶ containing statistical copolymer of PCHVE and PVA as the rigid phase. With 22 wt% of P(CHVE-stat-VA), polymers broke at 830 % strain with ultimate stress of 11.5 MPa. (**Table 1.6**, no. 22-23)

Similar to poly(alkyl acrylate), the T_g of poly(alkyl vinyl ether) could also be tuned with alkyl substituents of different lengths.⁷⁷ With poly(n-butyl vinyl ether) (PnBVE, T_g , ~ -55 °C) as the elastic block, ABA-type triblock copolymer with (PTCVE, T_g ~ 77 °C),⁷⁷ poly(tricyclodecyl vinyl ether)⁷⁸ and poly(2-adamantyl vinyl ether) (PADVE, T_g ~ 155 °C) as glassy blocks were synthesized by living cationic

Table 1.6: Mechanical properties of ABA triblock copolymer type TPEs – all vinyl ether polymers

No.	Hard Segment (T _g , °C)	Soft Segment (T _g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
22	 (88 °C)	 (-61 °C)	15.11MPa	800%	31%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C)	75
			9.16MPa	1300%	22%		
23	 (88 °C)	 (-61 °C)	24.5MPa	370%	44.7%	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C) Hydrolysis	76
			11.5MPa	830%	22%		
24	 (150 °C)	 (68 °C)	1.35MPa	116%	30.7%	Cationic PLZ (Toluene, 0 °C)	77
		 (70 °C)	0.74MPa	92%	27.6%		
25	 (77 °C)	 (-52 °C)	2.4MPa	90%	24.4%	Cationic PLZ (Toluene, 0 °C)	78
26	 (155 °C)	 (-52 °C)	5.55MPa	245%	30%	Cationic PLZ (Toluene, 0 °C)	79
			1.52MPa	355%	17.2%		

polymerization.⁷⁹ Despite the similarity of monomer structures, microphase separation was observed by transmission electron microscopy (TEM). All of these vinyl ether TPEs showed relatively low strain at break (<355 %) and ultimate stress (<5.55 MPa), possibly because of high entanglement molecular weight of PnBVE. All vinyl ether triblock copolymers with poly(6-acetoxyhexyl vinyl ether) and poly (2-(2-methoxyethoxy)ethyl vinyl ether) as elastic blocks showed excellent CO₂ separation ability with modest mechanical properties (**Figure 1.3**).⁷⁷ (**Table 1.6**, no. 24-26)

1.2.3 Polymers prepared by metal catalyzed ring opening polymerization:

Poly(lactide) (PLA, $T_g \sim 60^\circ\text{C}$) is an amorphous biodegradable polymer synthesized by metal catalyzed ring opening polymerization (ROP) from racemic D,L-lactide whereas isotactic poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semicrystalline polymers ($T_m \sim 170^\circ\text{C}$). Blends of PLLA and PDLA can form stereocomplex crystals which further improves chemical resistance with higher melting temperature ($T_m \sim 203^\circ\text{C}$).⁸⁰

In the early research stage about incorporating PLA as the end block for ABA triblock copolymers for TPE applications, difunctional hydroxyl terminated PI,⁸¹ PIB,⁸² polydimethylsiloxane (PDMS)⁸³ and poly(ethylene-co-propylene)⁸⁴ were used as the initiators. These elastic middle block were prepared by either living anionic or cationic polymerization followed by termination with hydroxyl functionality. TPEs based on these systems received limited success with relative low stress and strain at break (**Table 1.7**, no. 27-30).

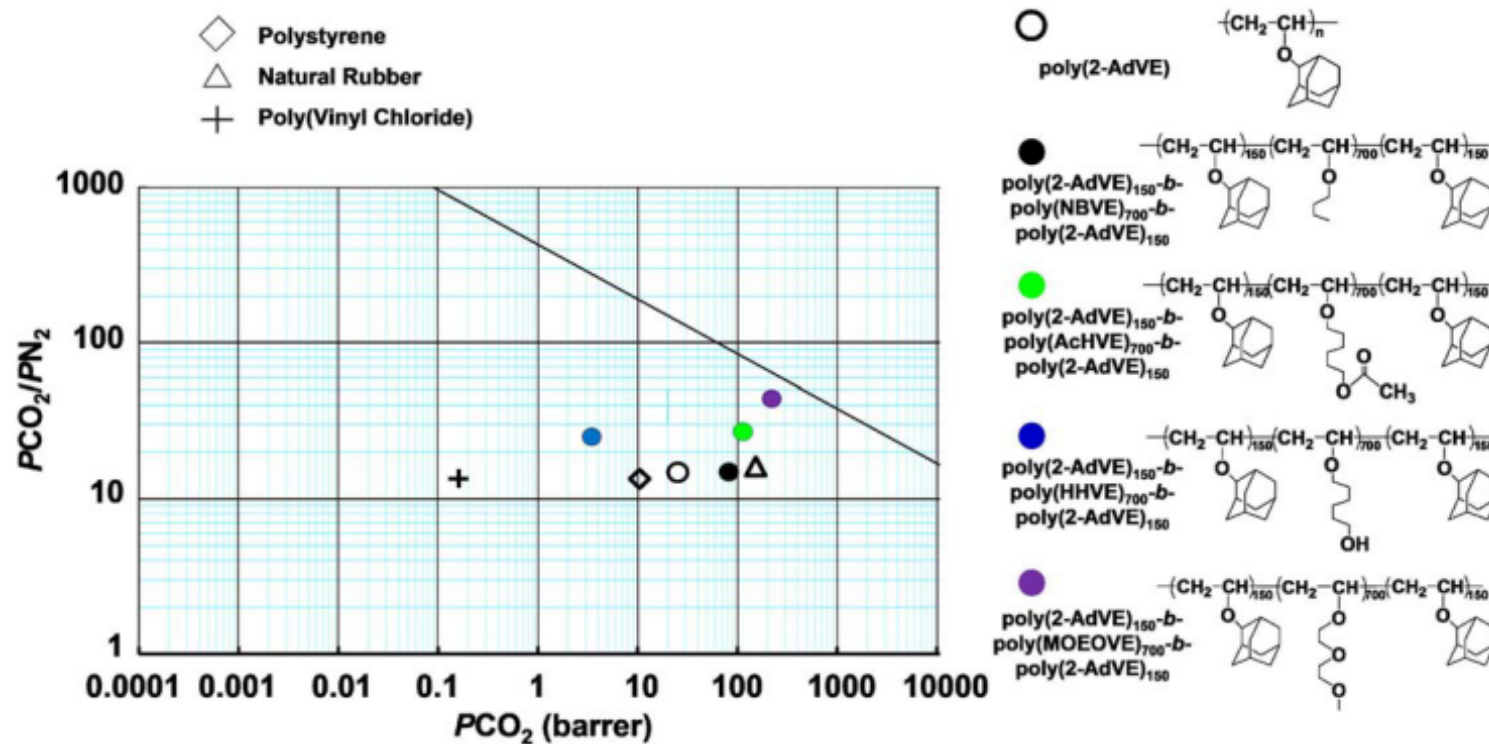

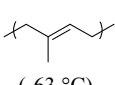

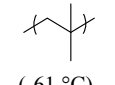

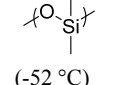

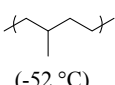


Figure 1.3: CO₂ separation plots for poly(6-acetoxihexyl vinyl ether) and poly (2-(2-methoxyethoxy)ethyl vinyl ether) based triblock copolymers together with commodity polymers [polystyrene, natural rubber, and poly(vinyl chloride)] for comparison.⁷


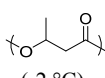

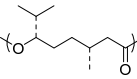

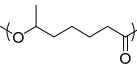

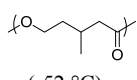

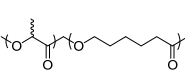

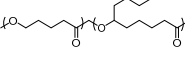

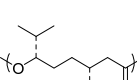
Table 1.7: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ring opening polymerization with PLA as the glassy segment.

No.	Hard Segment (T _g , °C)	Soft Segment (T _g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
27	 (60 °C)	 (-63 °C)	3.1 MPa	200%	18 vol%	Anionic PLZ (Toluene, 25 °C)	81
			9.2 MPa	650%	28 vol%	Metal Catalyzed ROP (Toluene, 125 °C)	
			10.1 MPa	450%	40 vol%		
28	 (60 °C)	 (-61 °C)	N/A	N/A	N/A	Cationic PLZ (CH ₃ Cl/MCHx, -80 °C) ROP (THF)	82
29	 (60 °C)	 (-52 °C)	N/A	N/A	N/A	Metal Catalyzed ROP (Toluene, 125 °C)	83
30	 (60 °C)	 (-52 °C)	2.98MPa	215%	45%	Anionic PLZ Catlytic Hydrogenation Metal Catalyzed ROP (Toluene, 125 °C)	84

Preparing polymers from renewable resource materials instead of from petroleum resources has been a lasting goal of chemists for many decades. Monomers including 3-hydroxybutyrate (HA), menthide (MD), 6-methyl- ϵ -caprolactone (MCL), ϵ -caprolactone (CL), β -methyl- δ -valerolactone (MCL), ϵ -decalactone (DL) potentially could be produced from sustainable resources.⁸⁵ These monomers undergo metal catalyzed ring opening polymerization (ROP), yielding biodegradable elastic polymers.^{86,87} Since ROP generated polymers with hydroxyl functionality on both ends, the resulting polymers could be directly used as macroinitiators for lactide, producing various types of biodegradable ABA triblock copolymer TPEs. When poly(3-hydroxybutyrate) (PHA)⁸⁸ was used as elastic block, TPEs had strain at break lower than 200 %. Using polymenthide^{89,90} (PM) as elastic block, the strain at break could be largely improved to 960% compared to PHA system but ultimate stress was decreased to 1.7 MPa even with 40 vol% of PLA. This low tensile stress might be due to the overall molecular weight not being high enough for strong phase separation. With 30 vol% of poly(6-methyl- ϵ -caprolactone)⁹¹ (PMCL) as the elastic block, 1880 % strain at break was achieved with 10.2 MPa ultimate stress (**Table 1.8**, no. 31-33).

Very recently, Xiong⁹² developed an economically viable strategy to prepare β -methyl- δ -valerolactone (MCL) through an artificial biosynthetic approach (**Figure 1.4**). Ring opening polymerization of MCL generated elastic amorphous aliphatic polyester with T_g of -52 °C. Excellent tensile properties were obtained by utilizing PMCL as the elastic block with PLA as the hard segment. With 32 vol% of PLA, PLA-

Table 1.8: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ring opening polymerization with sustainable recourse

No	Hard Segment (T _g , °C)	Soft Segment (T _g , °C)	Mechanical Properties			Synthetic Methods	Ref
			Stress / MPa	Strain / %	wt %		
31	 (50 ~ 80 °C)	 (-2 °C)	10MPa	200%	44%	Metal Catalyzed ROP (Toluene, 100 °C)	88
32	 (44 °C)	 (-26 °C)	1.7MPa	960%	40.7%	Metal Catalyzed ROP (Toluene, 100 °C)	89
33	 (45 °C)	 (-43 °C)	10.2MPa	1880%	30%	Metal Catalyzed ROP (Toluene, 110 °C)	91
			14.2MPa	1360%	34%		
34	 (45 °C)	 (-52 °C)	25MPa	1725%	32vol %	Metal Catalyzed ROP (Toluene, 110 °C)	92
35	 (T _m , 152 °C)	 (-30°C)	17MPa	2800%	20%	Metal Catalyzed ROP (Toluene, 110 °C)	93
			21MPa	1900%	33%		
36	 (45 °C)	 (-63 °C)	9.9MPa	2100%	17vol %	Metal Catalyzed ROP (Toluene, 110 °C)	94
			13.5MPa	1690%	21vol %		
			18MPa	1200%	32vol %		
37	 (170 ~190 °C)	 (-21 °C)	4.1MPa	1600%>	6vol%	Metal Catalyzed ROP (Toluene, 135 °C)	97
			10.6MPa	800%	15vol %		
			13.0MPa	730%	20vol %	ATRP (DMF, 65 °C)	

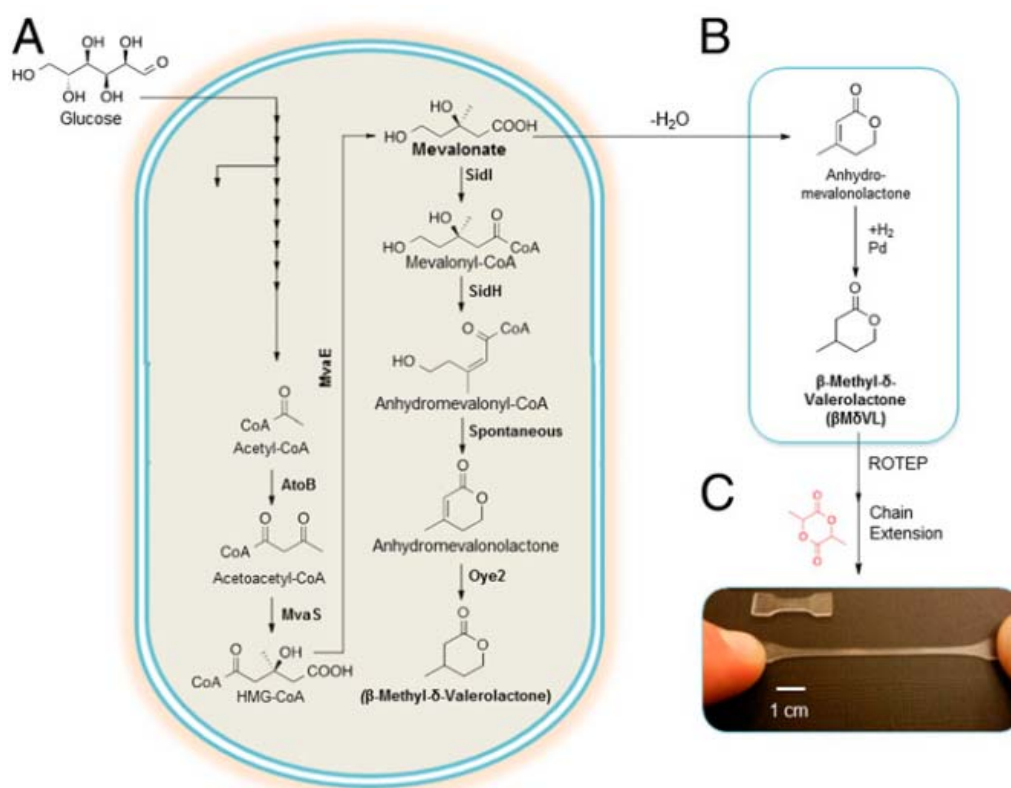


Figure 1.4: (a) Total biosynthetic pathway for the production of MVL. (b) A semisynthetic route to produce MVL from mevalonate. (c) Conversion of MVL to an elastomeric triblock polymer that can be repeatedly stretched to 18 times its original length without breaking.⁹²

PMCL-PLA triblock copolymer displayed 1725 % strain at break with ultimate stress of 25 MPa, which is competitive with commercial Kraton polymer based on petroleum resources (**Table 1.8**, no. 34).

As a low T_g semicrystalline polymer, poly(ϵ -caprolactone) (PCL, $T_g \sim -60^\circ\text{C}$, $T_m \sim 60^\circ\text{C}$) is a biodegradable material with great potential for medical applications. Copolymerizing ϵ -caprolactone with ϵ -decalactone or lactide created amorphous elastic polymers suitable for TPE applications.^{93,94} Statistical copolymer constructed from ϵ -caprolactone and D-lactide had a T_g of -30°C . With 20 wt% of isotactic poly(L-lactide) (PLLA) as the glassy block, triblock copolymers showed exceptionally high strain at break of 2800 % and decent ultimate stress of 17 MPa.⁹³ By varying volume fraction of the hard segment PLA from 17 % to 32 %, TPEs based on random copolymer of ϵ -caprolactone / ϵ -decalactone as soft segment demonstrated tunable ultimate stress from 9.9 MPa to 18 MPa with strain at break from 1200 % to 2100 %⁹⁴ (**Table 1.8**, no. 35-36).

Incorporating biodegradable PLA ($T_g \sim 60^\circ\text{C}$) enabled TPEs for many biomedical applications. However, high temperature applications are largely limited due to the low T_g of PLA. Poly(α -methylene- γ -butyrolactone) (PMBL) is a rigid thermoplastic⁹⁵ with a T_g of about 195°C . The renewable monomer MBL was derived from tulipalin A and subjected to radical polymerization⁹⁶. After converting dihydroxyl terminated poly(menthene) into difunctional atomic transfer radical polymerization initiator, PMBL-PM-PMBL⁹⁷ triblock type TPEs for high temperature

application were prepared. Ultimate tensile stress ranging from 3.9 MPa to 13 MPa and strain at break ranging from 730 % to 1800 % were achieved based on different volume fractions of PMBL (**Table 1.8**, no. 37).

1.2.4 Polymers prepared by controlled radical polymerization techniques:

Starting from the late 1990s, tremendous progress has been achieved in the field of controlled radical polymerization such as atomic transfer radical polymerization (ATRP), reversible addition-fragmentation chain-transfer polymerization (RAFT) and nitroxide mediated radical polymerization (NMRP).⁹⁸ These techniques open up various opportunities to prepare functionalized polymers with predictable molecular weight, narrow molecular weight distribution and complicated macromolecular architectures.⁹⁹ Controlled polymerization was achieved for many monomers such as acrylonitrile,¹⁰⁰ acrylamide¹⁰¹ and vinyl amide,¹⁰² which cannot be controllably polymerized by anionic or cationic mechanisms.

Many block, star, grafted and brush polymers with different functionalities have been prepared by ATRP.¹⁰³ However, ABA type block copolymers synthesized by ATRP have received limited success for TPE applications mainly due to two reasons: (1) broad distribution of hard block reduces the strength of phase separation, (2) unavoidable diblock copolymer mixture in triblock copolymers acted as plasticizer diminishing the phase boundary.^{39,48} Significantly lower tensile stress and strain were observed for PMMA-PnBA-PMMA triblock copolymers prepared by ATRP compared with triblock copolymers prepared by anionic polymerization followed by

tansalcoholysis.⁴⁸ The copolymerization of methyl methacrylate with α -methylene- γ -butyrolactone as glassy block was necessary to improve tensile properties of triblock copolymers with poly(n-butyl acrylate) as elastic block.¹⁰⁴ However, the ultimate stress was still lower than 3.2 MPa with strain at break of 650% (**Table 1.9**, no. 38).

Poly[2,5-bis[(n-hexogycarbonyl)]styrene] (PMPCS) is a mesogen-jacked liquid crystalline polymer with a T_g of about 120 °C. As a new type of rod-coil-rod TPE based on PMPCS and PnBA, tensile tests showed 1050 % strain at break with 3.2 MPa ultimate stress.¹⁰⁵ Different from PMPCS, poly2,5-bis[(n-hexogycarbonyl)]styrene (PHCS) is an amorphous polymer with a T_g of about -10 °C due to long chain alkyl substitution at the 2- and 5- positions of styrene. Poly(4-vinylpyridine) (P4VP) is a high T_g polymer that can complex with Zn^{2+} (**Figure 1.5**). Tuning stress-strain properties, glass transition temperature and morphology of TPEs based on P4VP-PHCS-P4VP was achieved by adding different amounts of $Zn(ClO_4)_2$ ¹⁰⁶ (**Table 1.9**, no. 39-40).

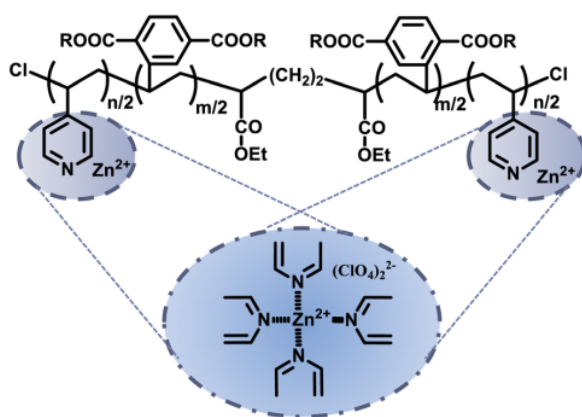


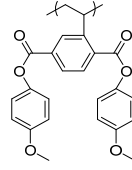


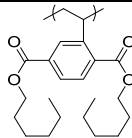





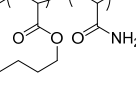


Figure 1.5: Illustration of a Zn^{2+} /VHV hybrid via metal-ligand complexation.¹⁰⁵

Table 1.9: Mechanical properties of ABA triblock copolymer type TPEs synthesized by ATRP

No	Hard Segment (T _g , °C)	Soft Segment (T _g , °C)	Mechanical Properties			Synthetic Methods	Ref
			Stress / MPa	Strain / %	wt %		
38	 (195 °C)	 (-50 °C)	0.5MPa	310%	13.8%	ATRP (DMF, 65°C)	104
39	 (119 °C)	 (-45 °C)	3.2MPa	1050%	37.58 %	ATRP (Chlorobenzene, 65°C)	105
40	 (60 °C)	 (-10 °C)	6.6MPa	400%	17%	ATRP (Chlorobenzene, 65°C)	106

In order to minimize undesired chain transfer and termination reactions, controlled radical polymerization needs to maintain a very low radical concentration. This increases reaction time compared to conventional free radical and ionic polymerization.¹⁰⁷ Radical segregation effect introduced by (mini)emulsion polymerization in heterogeneous system, on the other hand, reduced the reaction time and suppressed radical termination.^{108,109} Combining emulsion polymerization with RAFT, PS-PnBA-PS triblock copolymers with different molecular weight and composition were prepared in shorter reaction time.¹¹⁰ By varying weight percentage of PS from 20.2 % to 71.5 %, ultimate tensile strength was in the range from 3.0 MPa to 12.5 MPa and strain at break was in the range from 90 % to 1300 %. It was also found that by using a poly[styrene-alt-(maleic anhydride)] (PSM) as a macro-chain transfer agent in emulsion polymerization for PS-PnBA-PS¹¹¹, ultimate stress increased whereas strain at break decreased as the percentage of PSM increased. Another TPEs based on PS and poly(lauryl acrylate) were prepared by a solution of RAFT polymerization process.¹¹² Ultimate stress was lower than 1 MPa and strain at break was lower than 280 %. An interesting ABA triblock copolymer was prepared by RAFT polymerization based on P4VP as a hard segment and random copolymer of PnBA and poly(acrylamide) (PAM) as the elastic block. The PAM moiety in the middle block crosslinked the elastic domain through hydrogen bonding association.¹¹³ (**Table 1.10**, no. 41-43).

Table 1.10: Mechanical properties of ABA triblock copolymer type TPEs synthesized by RAFT polymerization

No.	Hard Segment (T_g , °C)	Soft Segment (T_g , °C)	Mechanical Properties			Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %		
41	 (95 °C)	 (-45 °C)	3.2MPa	1300%	20.2%	RAFT (H ₂ O, 70°C)	111
			7.0MPa	620%	36.1%		
			10.3MPa	520%	46.1%		
42	 (106 °C)	 (-23 °C)	3.2MPa	1050%	37.58 %	ATRP (Chlorobenzene, 65°C)	113
43	 (60 °C)	 (-10 °C)	6.6MPa	400%	17%	ATRP (Chlorobenzene, 65°C)	112

1.2.5 Polymers prepared by metathesis polymerization techniques:

Polyolefins represent almost two-thirds of global consumption of plastic and elastomer products. Ethylene and propylene are the two main feedstocks for polyolefins due to their low cost and availability. Linear polyethylene (PE), as well as isotactic and syndiotactic polypropylene (*i*-PP and *s*-PP) are semicrystalline polymers and could be employed as the hard segment for TPE applications. Atactic polypropylene (*a*-PP) and poly(ethylene-co-propylene) (PEP) are amorphous soft polymers and suitable for TPE's elastic segment.¹¹⁴

In 1959, Natta already proposed a possible TPE structure based on *i*-PP as the hard segment and *a*-PP as the soft segment.¹¹⁵ After almost half a century, in 2006, two different groups reported two kinds of TPEs based on ethylene and/or propylene monomers synthesized by living coordination polymerization (LCP). Sita¹¹⁶ used a specifically designed zirconium/borate complex for programmable stereomodulated living Ziegler-Natta polymerization. Simply by adjusting the zirconium/borate ratio and disrupting propylene feeding during the polymerization, diblock, triblock and tetrablock copolymers of *a*-PP and *i*-PP were prepared with 40 wt% of *i*-PP.

Coates¹¹⁷ prepared a nickel catalyst that produced *i*-PP at -60°C and *a*-PP at 0°C. Simply by changing the reaction temperature, *i*-PP-*b*-*a*-PP-*b*-*i*-PP triblock and *i*-PP-*b*-*a*-PP-*b*-*i*-PP-*b*-*a*-PP-*b*-*i*-PP pentablock copolymers were prepared. Triblock copolymer showed 1800 % strain at break with 40 MPa ultimate stress in tensile test, whereas pentablock copolymers showed 2250 % strain at break with ultimate stress of

240 MPa. The same group used titanium catalysts to prepare *s*-PP-*b*-PEP-*b*-*s*-PP triblock copolymers. The resulting triblock copolymer exhibited 80 MPa ultimate stress with 500 % strain at break. Very recently, Sita¹¹⁸ reported another triblock TPEs based on poly(1,3-methylenecyclohexane) (PMCH) and *a*-PP. Triblock copolymers of PMCH-*b*-*a*-PP-*b*-PMCH were prepared by LCP with hafnium catalysts (**Figure 1.6**). Interestingly, the rigid block PMCH was prepared by ring closing of 1,6-heptadiene, and the resulting polymer PMCH was micro-phase separated with *a*-PP (**Table 1.11**, no. 44-46).

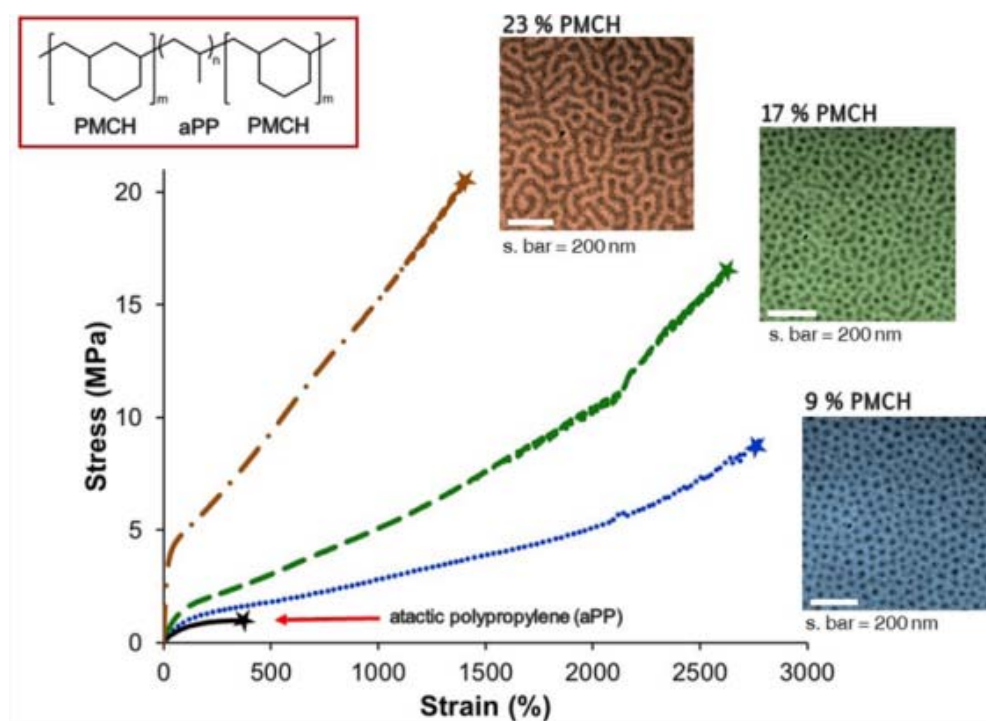










Figure 1.6: Triblock TPEs based on PMCH and *a*-PP.¹¹⁸

Table 1.11: Mechanical properties of ABA triblock copolymer type TPEs synthesized by coordination polymerization

No	Hard Segment (T_g , °C)	Soft Segment (T_g , °C)	Mechanical Properties			Synthetic Methods	Ref
			Stress / MPa	Strain / %	wt %		
44	 (T_m , 130 °C)	 (-45 °C)	18.5MPa	1227%	40%	LCP (Toluene, -10°C)	116
45	 (T_m , 130 °C)	 (-44 °C)	40MPa	1800%	24% (Triblock)	LCP (Toluene, 0°C/-60°C)	117
	 (T_m , 134 °C)	 (-57 °C)	240MPa	2250%	24% (Pentablock)		
			80MPa	500%	24%		
46	 (60 °C)	 (-10 °C)	8.9MPa	2773%	9vol%	LCP (Toluene, 0°C/-60°C)	118
			16.4MPa	2631%	17vol%		
			20.3MPa	1390%	23vol%		

1.3 Star branched polymers for TPEs:


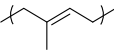

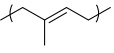
Star branched polymers are polymers with more than two arms radiating from the same core. If these arms have different chemical composition or molecular weight, the star polymer is named miktoarm (mixed-arm) star polymer. Generally, star polymers are prepared by two methods: (1) “Arm-first” where polymer arms are synthesized first and coupled onto a core decorated with appropriate reaction sites. (2) “Core first”, where polymer arms are grown from a multi-functional initiator.^{119,120}

When more than two PS-*b*-PI diblock copolymers are connected at the same core through the end of PI end blocks, with proper composition, such (PS-*b*-PI)_x star branched polymers displayed mechanical properties similar to SIS linear triblock TPEs. By using an arm-first divinylbenzene linking strategy, Fetters¹²¹ prepared polystyrene-polydiene star block copolymers with number of arms up to 29. They found these star polymers had superior tensile properties compared to linear triblock copolymers of similar composition. The enhancement of tensile strength saturated when the number of arms was more than six. Morphological analysis indicated for the same molecular weight, multi-arm star polymers had smaller PS domains size as compared with linear polymers¹²². Thus, star polymers had more condensed physical crosslinks per unit volume, which attributed to their higher tensile strength. Another reason for better tensile strength was that the core in star polymers acted as permanent crosslinks due to covalent chemical linkage. Besides better tensile stress of star polymers, the intrinsic viscosity of star polymers were lower than their linear analogues. PS/PI and PS/PB

diblock star copolymer TPEs are now commercially available under the trade name Kraton[®] (**Table 1.12**, no. 47).

Confirmed by both experiments¹²³ and theory¹²⁴, the morphological dependence of block copolymers could be decoupled from chemical composition by varying chain architecture. Progress in self-consistent field theory (SCFT)¹²⁵ facilitated the ability to design TPEs based on nonlinear architectures such as miktoarm star polymers with superior mechanical properties.¹²⁶ For SIS triblock copolymer, over 36 vol% of PS component leads to lamellar morphology which is unfavorable for TPE applications (**Figure 1.7**).¹²⁷ For A(BA')₄ miktoarm star polymer with one A block and 4 BA' block emanating from the same core, Fredrickson¹²⁶ predicted a stable morphology, of cylindrical A phase hexagonally dispersed in B matrix with volume fraction of A polymer up to 70%. As for experiments, miktoarm star polymer S(IS')₃ with 50 vol% of PS achieved stable cylindrical morphology.¹²⁸ High volume fraction of PS enabled this new types of TPE with a higher modulus, strength toughness and recoverable elasticity. While SIS' with 50 vol% of PS yield at low elongation indicated its thermoplastic nature (**Table 1.12**, no. 48). By blending with PS homopolymers, a new stiff TPE (modulus was 99.2 MPa) with aperiodic “bricks and mortar” mesophase morphology was achieved with up to 82 wt% of PS.¹²⁹ Using similar miktoarm star polymer by blending with PS, Lynd created lamellar morphology with up to 97 wt% of PS.¹³⁰

Table 1.12: Mechanical properties of star-branched polymer type TPEs synthesized by anionic polymerization

No.	Hard Segment (T _g , °C)	Soft Segment (T _g , °C)	Mechanical Properties			Architecture	Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %			
47	 (95 °C)	 (-64 °C)	33.8MPa	1110%	29%	SIS Linear	Anionic PLZ	121
			37.3MPa	1110%	29%	(SI) ₄ Star		
			39.2MPa	1030%	32%	(SI) ₇ Star		
			39.7MPa	1100%	33%	(SI) ₂₂ Star		
48	 (95 °C)	 (-64 °C)	12.6MPa	742%	40vol %	S(IS') ₃	Anionic PLZ	127
			11.3MPa	496%	50vol %			
			19.96MPa	294%	70vol %			

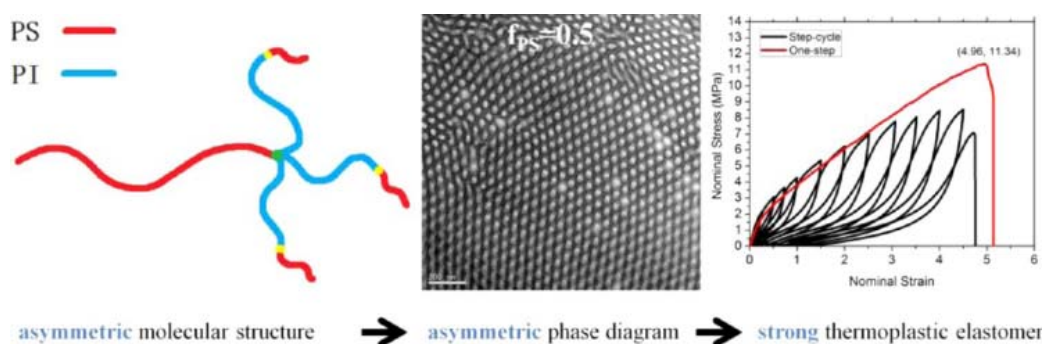


Figure 1.7: S(IS')₃ miktoarm star copolymer type TPEs.¹²⁸

For the “core-first” strategy: developing multifunctional anionic initiators received limited success mainly because of the poor solubility of such initiators in hydrocarbon solvents.¹³¹ However multifunctional initiators for cationic polymerization are possible. (PpCS-PIB)₈ eight arms star polymers were prepared through a calix[8]arene core with eight initiation sites.¹³² (PMMA-PIB)₃ three arms star polymers were prepared by a trifunctional cationic initiator followed by ATRP of MMA.¹³³ For the “arm-first” strategy: at the end of living cationic polymerization, vinyl functionality was introduced by reacting the living cation of PS-PIB⁺ and PID-PIB⁺ with allyltrimethylsilane. The vinyl end functionality further reacted with Si-H on cyclosiloxane by Pt catalyzed hydrosilylation and produced star polymers of (PS-PIB)_n and (PID-PIB)_n based on different numbers of Si-H on cyclosiloxane.^{134,135,136} Similar to arm first divinylbenzene linking strategy for anionic polymerization, 1,4-cyclohexane dimethanol divinyl ether was applied as the linking agent for arm first cationic polymerization to prepare star polymers with poly(2-admantyl vinyl ether) as

hard segment and poly(n-butyl vinyl ether) as elastic segment.⁷⁹ (**Table 1.13**, no. 49-53).

By using tri-functional ATRP initiator for “core first” strategy, three arms star polymers with PMMA,¹³⁷ polyacrylonitrile (PAN),¹³⁸ and PS¹³⁹ as glassy segment, PnBA as elastic segment were prepared for TPE properties evaluation. As an all acrylic TPE, three arm star (PMMA-PnBA)₃ with 36 % of PMMA showed 11 MPa ultimate stress with 545 % strain at break. (PAN-PnBA)₃ star polymers displayed ultimate tensile stress from 6.3 MPa to 12.7 MPa as the strain at break in the range from 382 % to 700 %. Phase separation between PAN and PnBA was retained when the temperature was below 250 °C. As temperature was further raised up to 280 °C, the PAN domain started to crosslink chemically, and the storage modulus of these materials dropped when temperature was close to 300 °C. With multifunctional ATRP initiator of 10 and 20 initiation sites, 10 arms and 20 arms PMBL/PnBA star polymers were prepared for high temperature TPE applications.¹⁴⁰ The highest ultimate tensile stress achieved was 7.8 MPa. Strain at break was lower than 140 % (**Table 1.14**, no. 54-57).

1.4 Grafted polymers for TPEs:

As an important class of commercial polymeric materials, graft copolymers are composed of a polymer backbone with polymer side chains attached to it. Grafted polymers can be prepared by three strategies: (1) “Grafting onto”, where both polymer backbone and side chain are pre-synthesized and then through the end functionalities on side chain and in-chain functionality on backbone, side chains are grafted onto the

Table 1.13: Mechanical properties of star-branched polymer type TPEs synthesized by cationic polymerization

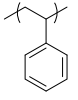
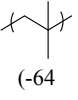
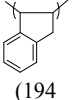
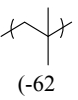


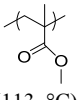
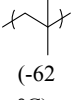
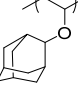
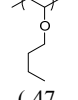








N o.	Hard Segme nt (T _g , °C)	Soft Segme nt (T _g , °C)	Mechanical Properties			Architect ure	Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %			
49	 (95 °C)	 (-64 °C)	18.1MPa	540%	23%	(PS-PIB) ₅ Star	Cationic PLZ	134,135
			20.2MPa	550%	23%	(PS-PIB) ₁₆ Star		
			21.1MPa	560%	23%	(PS-PIB) ₂₁ Star		
50	 (194 °C)	 (-62 °C)	12.7MPa	545%	23%	(PID-PIB) ₅ Star	Cationic PLZ	136
			16.8MPa	550%	23%	(PID-PIB) ₂₁ Star		
51	 (127 °C)	 (-62 °C)	22-27MPa	400-650%	23-31%	(PpCS-PIB) ₈ Star	Cationic PLZ	132
52	 (113 °C)	 (-62 °C)	22.5MPa	125%	31.7%	(PMMA-PIB) ₃ Star	Cationic PLZ ATRP	133
53	 (165 °C)	 (-47 °C)	6.9MPa	330%	21.1%	(PADVE-PnBVE) ₈₀ Star	Cationic PLZ	79


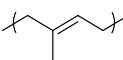

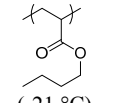
Table 1.14: Mechanical properties of star-branched polymer type TPEs synthesized by ATRP

No.	Hard Segment (T_g , °C)	Soft Segment (T_g , °C)	Mechanical Properties			Architecture	Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %			
54	 (131 °C)	 (-51 °C)	11MPa	545%	36%	(PMMA-PnBA) ₃ Star	ATRP	137
55	 (105 °C)	 (-50 °C)	6.8MPa	700%	11%	(PAN-PnBA) ₃ Star	ATRP	138
			6.3MPa	440%	15%			
			12.7MPa	382%	22%			
56	 (117 °C)	 (-21 °C)	2.35MPa	700%	20.5 %	(PS-PnBA) ₃ Star	ATRP	139
57	 (117 °C)	 (-21 °C)	7.8MPa	140%	24.2 %	(PMBL-PnBA) ₁₀ Star	ATRP	140

polymer backbones. (2) “Grafting from”, where multifunctional polymer backbones serve as the macroinitiator and initiated the polymerization of side chain monomers to graft from the backbone. (3) “Grafted through” or “macromonomer” approaches”, where polymer side chains having a polymerizable end group are synthesized, and those macromonomers are subsequently polymerized to form the backbone creating graft polymer.^{141,142,143,144}

By using anionic polymerization followed by polycondensation, Mays and co-workers prepared a series of grafted polymers with regular spaced trifunctional, tetrafunctional and hexafunctional junction points where PI was the backbone and PS was the side chain.^{145,146} Structure-property relationship of these grafted polymers were elucidated by characterizing morphology^{147,148} and mechanical properties^{149,150,151} of grafted polymers with different compositions (14 to 23 vol% of PS) and architectures (trifunctional, tetrafunctional and hexafunctional junction points). From their research, multigraft polymers with tetrafunctional junction points showed 1550 % strain at break which is 500% higher than that for the commercial product Kraton 1102. This superelasticity is a consequence of having the PI backbone anchored by multiple PS physical crosslinks (**Figure 1.8**). Both tetra- and hexafunctional multigraft polymers displayed higher elasticity than commercial TPE’s like Kraton or Styroflex. Polymers with more functionalities at one junction point had higher tensile stress and modulus (**Table 1.15**, no. 58).

Table 1.15: Mechanical properties of grafted polymer type TPEs synthesized by anionic polymerization

No	Side Chain (T _g , °C)	Backbone (T _g , °C)	Mechanical Properties			Architecture*	Synthetic Methods	Ref.
			Stress / MPa	Strain / %	wt %			
58	 (95 °C)	 (-51 °C)	6.39MPa	1386%	17vol %	MG-3-17-3.7	Anionic PLZ	149
			14.15MPa	1550%	14vol %	MG-4-14-3.5		
			14.63MPa	1373%	21vol %	MG-6-21-5.2		
59	 (117 °C)	 (-21 °C)	0.05MPa	>500%	26%	MG-3-26-9.2	Anionic PLZ	152
			0.55MPa	450%	22%	MG-3-22-5.3	RAFT	

*MG-n-m-x, n is the number of functionality of then junction point, m is the weight percentage of hard segment, x is the average number of junction points.

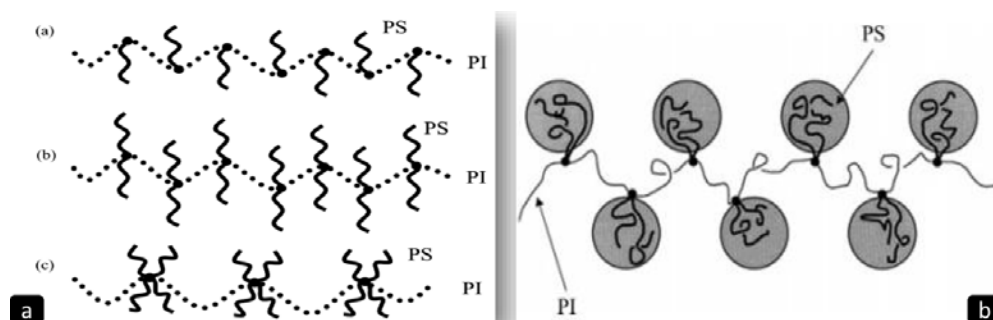


Figure 1.8: a). Illustration of multigrafted copolymers based on PI backbone and PS branches. b). Chain conformation of multigrafted copolymers in microphase-separated state.¹⁴³

Inspired by this work, the same group prepared graft all acrylic TPEs based on PMMA side chain and PnBA backbone.¹⁵² The PMMA macromonomers were synthesized by living anionic polymerization and copolymerized with nBA by RAFT polymerization. Similar to other linear and star all acrylic TPEs, low modulus and stress was found in PnBA-g-PMMA graft polymers due to high M_e of PnBA and phase blending between PMMA and PnBA. Zhang and Mays further extended the versatilities of graft polymer architecture by a cost efficient process combining (mini)emulsion polymerization with anionic polymerization or ATRP to prepare trifunctional and tetrafunctional grafted copolymers with PS or PMMA as side chain, PI or PnBA as the backbone.^{153,154,155,156} However, mechanical properties of these materials from tensile test were not presented (**Table 1.15**, no. 59).

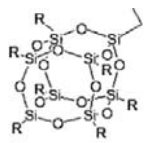
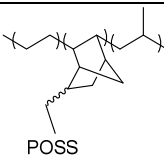
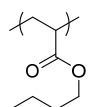
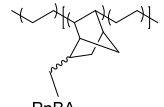
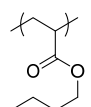
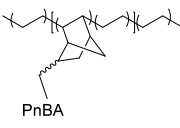
Polyhedral oligomeric silsesquioxanes (POSS) are silicon containing organic-inorganic materials.¹⁵⁷ Hybrid materials with silicone combines thermal /oxidative resistance from inorganic materials and processability of organic materials.¹⁵⁸ Copolymerizing ethylene and propylene with ethyl-POSS-norbornene by coordination

polymerization produced random terpolymers of ethylene-propylene-silsesquioxane.¹⁵⁹ High stress (>10 MPa) was observed for these silica containing TPEs. Similar research conducted by Bazan¹⁶⁰, which copolymerized ethylene with 5-norbornene-2-bromo-2-methylpropanoate (NBMP) which yielded a PE backbone with randomly distributed 2-bromo-2-methylpropanoate as ATRP initiator. Further grafting n-Butyl acrylate by ATRP produced PE-g-PnBA TPEs with 15 MPa ultimate stress and 490 % strain at break. The same group further prepared PE-b-(PE-co-PNBMP)-b-PE, a triblock copolymer with PE at both end and macroinitiator in the middle block.¹⁶¹ Graft polymers showed ultimate tensile stress of 27 MPa with 1310 % strain at break (**Table 1.16**, no. 60-62).

Traditionally there are two types of macromolecular architectures that form a continuous rubbery matrix and suitable for TPEs: (1) linear and star polymers with glassy end (out) block and elastic middle (inner) block (architecture I); (2) graft polymers with elastic backbone and rigid side chain (architecture II). Tang and Wang¹⁶² proposed a reversed graft architecture with elastic side chain grafted on rigid backbone (architecture III, **Figure 1.9**). Notice that in architecture III, the backbone does not necessarily need to be a glassy polymers. Rigid polymers and inorganic materials such as cellulose,^{162,163,164,165} carbon nanotubes^{166,167} and even iron magnetic particles¹⁶⁸ could be used as backbone.

In order to validate the effectiveness of architecture III, ATRP-initiator-functionalized rigid cellulose was prepared with different number of initiation sites.¹⁶²

Table 1.16: Mechanical properties of grafted polymer type TPEs synthesized by ring opening metathesis polymerization

No	Side Chain	Backbone	Mechanical Properties			Synthetic Methods	Ref
			Stress / MPa	Strain / %	wt %		
60		 POSS	10.2MPa	723%	21%	Coordination PLZ	159
			13.4MPa	448%	30%		
			19.3MPa	450%	36%		
61		 PnBA	15MPa	490%	11%	Coordination PLZ	160
			3MPa	780%	28%	ATRP	
			0.9MPa	1170%	29%		
62		 PnBA	20MPa	2000%	72%	Coordination PLZ	161
						ATRP	

MMA and nBA was randomly copolymerized on the cellulose backbone in DMF at 70 °C. Compared with linear, star and grafted all acrylic TPEs, architecture III type all acrylic TPEs displayed higher ultimate stress (11.1 MPa) with modest strain at break (550 %). Another reason for high stress was attributed to the hydrogen bonding between the carbonyl group on acrylic side chains and hydroxyl groups on cellulose. Microphase separation was observed between all acrylic side chain and cellulose backbone. Sustainable TPEs with monomers derived from rosin and fatty acids were prepared by the same strategy.¹⁶⁴

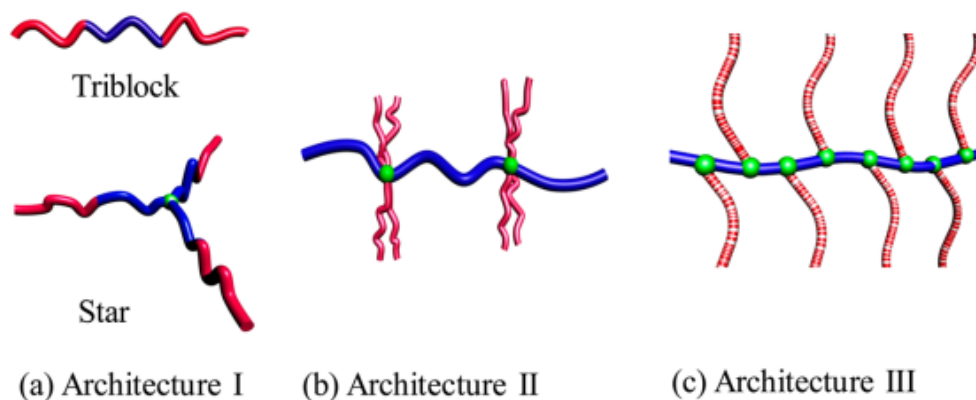


Figure 1.9: Illustration of TPEs' architecture¹⁶²

Grafting polyisoprene onto the backbone of cellulose was achieved by Wang,¹⁶³ and the resulting materials could mimic mechanical properties of human skin (**Figure 1.10**).¹⁶⁵ Different from cellulose-g-(PnBA-co-PMMA), for which only one T_g corresponding to (PnBA-co-PMMA) was reported, two distinguishable T_g s were observed through dynamic mechanical analysis in cellulose-g-PI. (**Table 1.17**, no. 63-

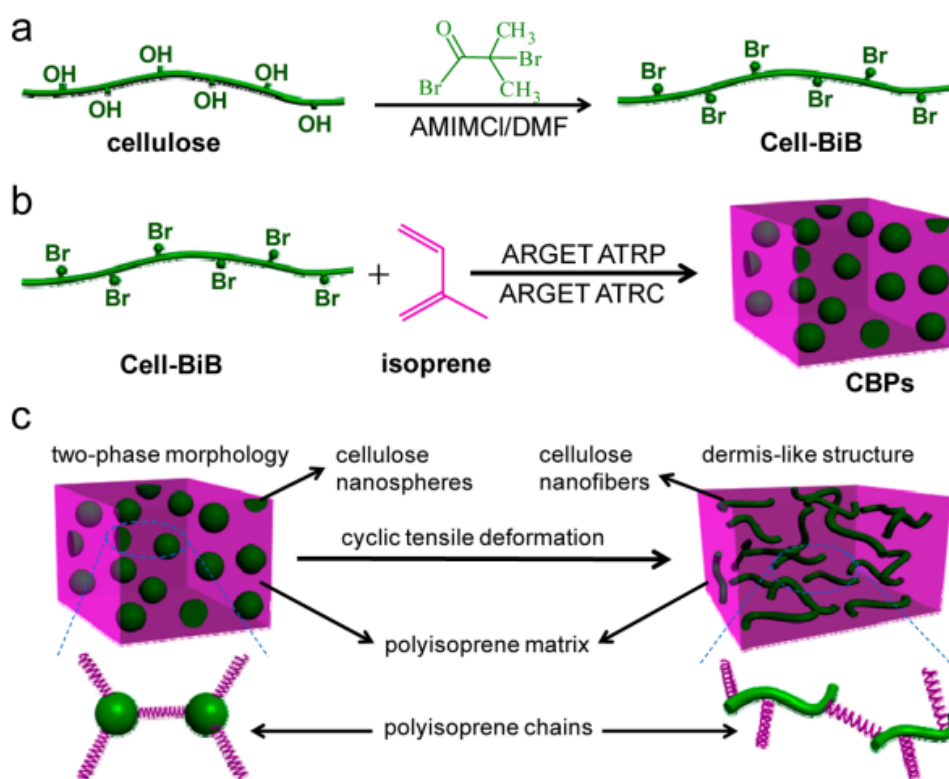
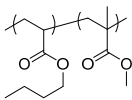
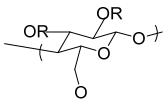
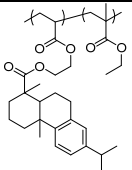
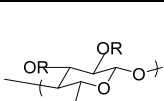
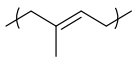
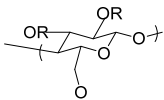
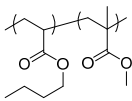

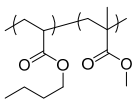
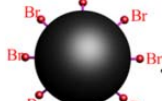


Figure 1.10: Design concept and synthesis of nanostructured elastomers mimicking the mechanical properties of human skin. (a) ATRP macroinitiator, (b) Cross-linked brush polymers were synthesized and self-assembled into two-phase morphology. (c) Two phase morphology of CBPs can be reconfigured into that close to the skin microstructure model.¹⁶³

Table 1.17: Mechanical properties of grafted polymer type TPEs based on architecture III

No	Side Chain	Backbone	Mechanical Properties			Synthetic Methods	Ref
			Stress / MPa	Strain / %	wt %		
63		 Side Chain	2.3MPa	1000%	39.6 %	ATRP	162
			6.6MPa	660%	47.5 %		
			11.1MPa	550%	54.8 %		
64		 Side Chain	0.25MPa	1000%	20%	ATRP	164
			2.0MPa	500%	30%		
65		 Side Chain	9.7MPa	160%	4.3%	ATRP	165
			32MPa	60%	20.6 %		
66		 Carbon Nanotube	2.4MPa	951%	0%	ATRP	166
			7.8MPa	520%	1.7%		
			9.9MPa	293%	3.8%		
67		 Fe ₃ O ₄ Nano particle	3.5MPa	921%	1.3%	ATRP	168
			9.0MPa	641%	2.8%		
			14.6MPa	458%	1.3%		

65). By replacing cellulose with functionalized carbon nanotubes (CNT) and Fe_3O_4 nanoparticles (NPs), TPEs with type III architecture were successfully prepared. When carbon nanotubes¹⁶⁶ were used as the rigid segment, 1.7 % of CNT loading increased the ultimate tensile stress from 2.4 MPa to 7.8 MPa. Strain at break was reduced from 951 % to 520 %. TPEs with Fe_3O_4 showed recyclability under magnetic field.¹⁶⁸ (**Table 1.17**, no. 66-67)

1.5 Perspective:

The past 60 years has witnessed rapid development of thermoplastic elastomers from discoveries in the laboratory to widely applied commodities involved in everyone's daily life. Starting from the 21 century, progress made in different polymerization techniques has advanced new types of TPEs with various chemical compositions and macromolecular architectures. However, each polymerization technique has both merits and weakness.

Kraton styrenic thermoplastic elastomers are the most commercially successful polymeric materials synthesized by living anionic polymerization. The disadvantage of S-TPEs is obvious: low service temperature and poor UV/oxidation resistance. All acrylic TPEs show better chemical resistance, however, the mechanical properties of these materials are much lower than those of S-TPEs.

Cationic polymerization was used to prepare PIB based TPEs showing higher service temperature with better chemical resistance. The problem for cationic polymerization is the low polymerization temperature, which is not favorable for

industrial applications. Low polymerization temperature also limited large scale production of (methyl) acrylate based TPEs by anionic polymerization.

Metal catalyzed ring opening polymerization produced biodegradable polymers from sustainable resources. However, most metal catalyzed ROP need toxic tin as the catalyst. Atomic transfer radical polymerization needs to reduce the radical concentration in order to control the polymerization. Polymers prepared by ATRP generally contain residual metal catalyst. Terminating the reaction at low conversion is necessary for block polymers preparation by ATRP.

Well defined PI-g-(PS)_n (n=1,2,3) showed great mechanical properties competitive with Kraton products. However, these anionically prepared polymers required laborious synthetic procedures. As one of the most favorable polymerization techniques in industry, emulsion polymerization offers many benefits: polymers with high weight average molecular could be prepared quickly in water as the reaction medium. Particles of polymers could be directly applied for coating and painting without purification. Recent research using macromonomer approaches to synthesize PI-g-PS by a combination of anionic polymerization and emulsion polymerization opens up opportunities to prepare thermoplastic elastomers by a cost efficient strategy. However, the PS macromonomer was prepared by anionic polymerization. Living anionic polymerization required oxygen and moisture free environment in order to retain the reactivity of chain end anion. Thrilling opportunities are waiting if PS

macromonomer could be prepared by all emulsion process with more than one branch points in the same macromonomer.

References:

- [1]. Bonart, R. *Polymer* **1979**, 20 (11), 1389-1403.
- [2]. Spontak, R. J.; Patel, N. P. *Current Opinion in Colloid & Interface Science* **2000**, 5 (5-6), 333-340.
- [3]. Shanks, R. A., General purpose elastomers: Structure, chemistry, physics and performance. In *Advances in Elastomers I*, Springer: 2013; pp 11-45.
- [4]. Walker, B. M.; Rader, C. P., *Handbook of thermoplastic elastomers*. Van Nostrand Reinhold New York: 1979.
- [5]. Drobny, J. G., *Handbook of thermoplastic elastomers*. Elsevier: 2014.
- [6]. Bhowmick, A. K.; Stephens, H., *Handbook of elastomers*. CRC Press: 2000.
- [7]. Fakirov, S., *Handbook of condensation thermoplastic elastomers*. John Wiley & Sons: 2006.
- [8]. Legge, N. R.; Holden, G.; Schroeder, H., Thermoplastic elastomers: a comprehensive review. *Carl Hanser Verlag, Kolbergerstr. 22, D-8000 Munchen 80, FRG, 1987. 574* **1987**.
- [9]. Matuszak, M. P., Production of isooctanes from cyclopropane and isobutane. U.S. Patent 2,632,031.: 17 Mar. 1953.
- [10]. Langerak, E. O.; Prucino, L. J.; Remington, W. R., Elastomers from polyalkylene ether glycol reacted with arylene diisocyanate and water. Patent No. 2,692,873. : 1954.

- [11]. S., S. C., Simulated vulcanizates of polyurethane elastomers. U.S. Patent 2,871,218, : 1959.
- [12]. Geoffrey, H.; Ralph, M., Block polymers of monovinyl aromatic hydrocarbons and conjugated dienes. U.S. Patent No. 3,265,765: 1966.
- [13]. Hsieh, H. Q., R. P., *Anionic polymerization: principles and practical applications*. . CRC Press: : 1996.
- [14]. Handlin, D. L. T., S.; Wright, K., Applications of Thermoplastic Elastomers Based on Styrenic Block Copolymers In *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*, Matyjaszewski, K. G., Y.; Leibler, L., Eds. , Ed. Wiley-VCH: 2007; Vol. 4, pp 2001-2031.: 2007.
- [15]. Szwarc, M., "Living" polymers. **1956**.
- [16]. Hirao, A.; Goseki, R.; Ishizone, T. *Macromolecules* **2014**, 47 (6), 1883-1905.
- [17]. Orlov, Y., Polymer thermodynamics: Leverage modeling results for industrial applications. In *Polymer Reaction Engineering IX*, E. Vivaldo-Lima, U. J. D., BASF; F. Zaldo-Garcia, CP-COMEX; J. Tsavalas,, Ed. ECI Symposium Series,: Univ. of New Hampshire Eds, , 2015.
- [18]. Drolet, F.; Fredrickson, G. H. *Physical Review Letters* **1999**, 83 (21), 4317.
- [19]. Iwao, T., Polymer solutions: An introduction to physical properties. New York: Wiley: 2002.
- [20]. Quirk, R. P., *Applications of anionic polymerization research*. American Chemical Society; Distributed by Oxford University Press: 1998.

- [21]. [http://www.grandviewresearch.com/industry-analysis/thermoplastic-elastomers-](http://www.grandviewresearch.com/industry-analysis/thermoplastic-elastomers-market)market Thermoplastic Elastomers (TPE) Market Analysis By Product (Styrenic Block Copolymers (SBC, SBS, SIS, HSBC).
- [22]. Karl, M.; Richard, H., Composition of matter comprising polypropylene and an ethylene-propylene copolymer. U.S. Patent No. 3,262,992.: 1966.
- [23]. Coran, A. Y.; Patel, R. P., Elastoplastic compositions of butyl rubber and polyolefin resin. U.S. Patent No. 4,130,534.: 1978.
- [24]. Hadjichristidis, N.; Hirao, A., *Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications*. Springer: 2015.
- [25]. Aoshima, S.; Kanaoka, S. *Chemical reviews* **2009**, *109* (11), 5245-5287.
- [26]. Matyjaszewski, K.; Tsarevsky, N. V. *Journal of the American Chemical Society* **2014**, *136* (18), 6513-6533.
- [27]. Khosravi, E.; Szymanska-Buzar, T., *Ring opening metathesis polymerisation and related chemistry: state of the art and visions for the new century*. Springer Science & Business Media: 2012; Vol. 56.
- [28]. Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49* (5), 1079-1131.
- [29]. Hawker, C. J.; Bosman, A. W.; Harth, E. *Chemical Reviews* **2001**, *101* (12), 3661-3688.
- [30]. G. Holden, N. R. L., Styrenic Thermoplastic Elastomers. In *Thermoplastic Elastomers*, Holden, G., Ed. Carl Hanser Verlag GmbH & Co;: 1996.

- [31]. Morton, M.; McGrath, J. E.; Juliano, P. C. *Journal of Polymer Science Part C: Polymer Symposia*, Wiley Online Library: 1969; pp 99-115.
- [32]. Fetters, L. J.; Morton, M. *Macromolecules* **1969**, *2* (5), 453-458.
- [33]. Bolton, J. M.; Hillmyer, M. A.; Hoyer, T. R. *ACS Macro Letters* **2014**, *3* (8), 717-720.
- [34]. Fetters, L.; Firer, E.; Dafaoui, M. *Macromolecules* **1977**, *10* (6), 1200-1207.
- [35]. Kobayashi, S.; Matsuzawa, T.; Matsuoka, S.-i.; Tajima, H.; Ishizone, T. *Macromolecules* **2006**, *39* (18), 5979-5986.
- [36]. Kobayashi, S.; Kataoka, H.; Ishizone, T.; Kato, T.; Ono, T.; Kobukata, S.; Ogi, H. *Macromolecules* **2008**, *41* (14), 5502-5508.
- [37]. Hucul, D. A.; Hahn, S. F. *Advanced Materials* **2000**, *12* (23), 1855-1858.
- [38]. Alfonzo, C. G.; Fleury, G.; Chaffin, K. A.; Bates, F. S. *Macromolecules* **2010**, *43* (12), 5295-5305.
- [39]. Yu, J. M.; Dubois, P.; Teyssié, P.; Jérôme, R. *Macromolecules* **1996**, *29* (19), 6090-6099.
- [40]. Yu, J. M.; Dubois, P.; Jérôme, R. *Macromolecules* **1996**, *29* (26), 8362-8370.
- [41]. Yu, J. M.; Dubois, P.; Jérôme, R. *Macromolecules* **1996**, *29* (23), 7316-7322.
- [42]. Bywater, S.; Worsfold, D. *Canadian Journal of Chemistry* **1967**, *45* (16), 1821-1824.
- [43]. Yu, Y.; Dubois, P.; Teyssié, P.; Jérôme, R. *Macromolecules* **1997**, *30* (15), 4254-4261.

- [44]. Yu, J.; Dubois, P.; Jérôme, R. *Macromolecules* **1997**, *30* (21), 6536-6543.
- [45]. Yu, J. M.; Dubois, P.; Jérôme, R. *Macromolecules* **1997**, *30* (17), 4984-4994.
- [46]. Yu, Y.; Dubois, P.; Jérôme, R.; Teyssié, P. *Journal of Polymer Science Part A: Polymer Chemistry* **1996**, *34* (11), 2221-2228.
- [47]. Varshney, S.; Kesani, P.; Agarwal, N.; Zhang, J.; Rafailovich, M. *Macromolecules* **1999**, *32* (1), 235-237.
- [48]. Tong, J.; Jérôme, R. *Polymer* **2000**, *41* (7), 2499-2510.
- [49]. Moineau, C.; Minet, M.; Teyssié, P.; Jérôme, R. *Macromolecules* **1999**, *32* (25), 8277-8282.
- [50]. Tong, J.-D.; Moineau, G.; Leclere, P.; Brédas, J.-L.; Lazzaroni, R.; Jérôme, R., *Macromolecules* **2000**, *33* (2), 470-479.
- [51]. Tong, J.-D.; Jérôme, R. *Macromolecules* **2000**, *33* (5), 1479-1481.
- [52]. Tong, J.-D.; Leclère, P.; Rasmont, A.; Brédas, J.-L.; Lazzaroni, R.; Jérôme, R. *Macromolecular Chemistry and Physics* **2000**, *201* (12), 1250-1258.
- [53]. Leclère, P.; Rasmont, A.; Brédas, J.-L.; Jérôme, R.; Aime, J.; Lazzaroni, R. In *Phase - separated microstructures in "all - acrylic " thermoplastic elastomers*, Macromolecular Symposia, Wiley Online Library: 2001; pp 117-137.
- [54]. Tong, J.; Leclère, P.; Doneux, C.; Brédas, J.-L.; Lazzaroni, R.; Jérôme, R. *Polymer* **2001**, *42* (8), 3503-3514.
- [55]. Chatterjee, D. P.; Mandal, B. M. *Macromolecules* **2006**, *39* (26), 9192-9200.
- [56]. Natori, I. *Macromolecules* **1997**, *30* (12), 3696-3697.

- [57]. Hong, K.; Mays, J. W. *Macromolecules* **2001**, *34* (4), 782-786.
- [58]. Imaizumi, K.; Ono, T.; Natori, I.; Sakurai, S.; Takeda, K. *Journal of Polymer Science Part B: Polymer Physics* **2001**, *39* (1), 13-22.
- [59]. Natori, I.; Imaizumi, K.; Yamagishi, H.; Kazunori, M. *Journal of Polymer Science Part B: Polymer Physics* **1998**, *36* (10), 1657-1668.
- [60]. Kosaka, Y.; Kitazawa, K.; Inomata, S.; Ishizone, T. *ACS Macro Letters* **2013**, *2* (2), 164-167.
- [61]. Kosaka, Y.; Kawauchi, S.; Goseki, R.; Ishizone, T. *Macromolecules* **2015**, *48* (13), 4421-4430.
- [62]. Wang, W., HighTemperature Thermoplastic Elastomers Synthesized by Living Anionic Polymerization in Hydrocarbon Solvent at Room Temperature. (Unpublished)
- [63]. Wang, W., Polybenzofulvene Based Thermoplastic Elastomer: Effects of Partial and Complete Hydrogenation. (Unpublished)
- [64]. Kennedy, J. P., Thermoplastic Elastomers by Carbocationic Polymerization. In *Thermoplastic Elastomers*, G. Holden, N. R. L., R. Quirk, H.E. Schroeder, Ed. Hanser Publishers: New York, 1996.
- [65]. Kaszas, G.; Puskas, J.; Kennedy, J.; Hager, W. *Journal of Polymer Science Part A: Polymer Chemistry* **1991**, *29* (3), 427-435.
- [66]. Cao, X.; Faust, R. *Macromolecules* **1999**, *32* (17), 5487-5494.

- [67]. Tsunogae, Y.; Kennedy, J. *Journal of Polymer Science Part A: Polymer Chemistry* **1994**, 32 (3), 403-412.
- [68]. Cao, X.; Sipos, L.; Faust, R. *Polymer Bulletin* **2000**, 45 (2), 121-128.
- [69]. Puskas, J.; Kaszas, G.; Kennedy, J.; Hager, W. *Journal of Polymer Science Part A: Polymer Chemistry* **1992**, 30 (1), 41-48.
- [70]. Li, D.; Faust, R. *Macromolecules* **1995**, 28 (14), 4893-4898.
- [71]. Kennedy, J.; Kurian, J. *Journal of Polymer Science Part A: Polymer Chemistry* **1990**, 28 (13), 3725-3738.
- [72]. Kennedy, J. P.; Price, J. L.; Koshimura, K. *Macromolecules* **1991**, 24 (25), 6567-6571.
- [73]. Kennedy, J.; MIDHA, S.; Tsunogae, Y. *Macromolecules* **1993**, 26 (3), 429-435.
- [74]. Fodor, Z.; Kennedy, J. *Polymer Bulletin* **1992**, 29 (6), 697-704.
- [75]. Zhou, Y.; Faust, R.; Chen, S.; Gido, S. P. *Macromolecules* **2004**, 37 (18), 6716-6725.
- [76]. Zhou, Y.; Faust, R.; Richard, R.; Schwarz, M. *Macromolecules* **2005**, 38 (20), 8183-8191.
- [77]. Hashimoto, T.; Imaeda, T.; Irie, S.; Urushisaki, M.; Sakaguchi, T. *Journal of Polymer Science Part A: Polymer Chemistry* **2015**, 53 (9), 1114-1124.
- [78]. Hashimoto, T.; Namikoshi, T.; Irie, S.; Urushisaki, M.; Sakaguchi, T.; Nemoto, T.; Isoda, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2008**, 46 (5), 1902-1906.

- [79]. Imaeda, T.; Hashimoto, T.; Irie, S.; Urushisaki, M.; Sakaguchi, T. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51* (8), 1796-1807.
- [80]. Pan, P.; Inoue, Y. *Progress in Polymer Science* **2009**, *34* (7), 605-640.
- [81]. Frick, E. M.; Zalusky, A. S.; Hillmyer, M. A. *Biomacromolecules* **2003**, *4* (2), 216-223.
- [82]. Sipos, L.; Zsuga, M.; Deák, G. *Macromolecular rapid communications* **1995**, *16* (12), 935-940.
- [83]. Zhang, S.; Hou, Z.; Gonsalves, K. *Journal of Polymer Science Part A: Polymer Chemistry* **1996**, *34* (13), 2737-2742.
- [84]. Huang, Y.; Pan, P.; Shan, G.; Bao, Y. *RSC Advances* **2014**, *4* (89), 47965-47976.
- [85]. Belgacem, M. N.; Gandini, A., *Monomers, polymers and composites from renewable resources*. Elsevier: 2011.
- [86]. Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Transactions* **2010**, *39* (36), 8363-8376.
- [87]. Hillmyer, M. A.; Tolman, W. B. *Accounts of chemical research* **2014**, *47* (8), 2390-2396.
- [88]. Hiki, S.; Miyamoto, M.; Kimura, Y. *Polymer* **2000**, *41* (20), 7369-7379.
- [89]. Wanamaker, C. L.; O'Leary, L. E.; Lynd, N. A.; Hillmyer, M. A.; Tolman, W. B. *Biomacromolecules* **2007**, *8* (11), 3634-3640.
- [90]. Wanamaker, C. L.; Bluemle, M. J.; Pitet, L. M.; O'Leary, L. E.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2009**, *10* (10), 2904-2911.

- [91]. Martello, M. T.; Hillmyer, M. A. *Macromolecules* **2011**, *44* (21), 8537-8545.
- [92]. Xiong, M.; Schneiderman, D. K.; Bates, F. S.; Hillmyer, M. A.; Zhang, K. *Proceedings of the National Academy of Sciences* **2014**, *111* (23), 8357-8362.
- [93]. Nakayama, Y.; Aihara, K.; Yamanishi, H.; Fukuoka, H.; Tanaka, R.; Cai, Z.; Shiono, T. *Journal of Polymer Science Part A: Polymer Chemistry* **2015**, *53* (3), 489-495.
- [94]. Schneiderman, D. K.; Hill, E. M.; Martello, M. T.; Hillmyer, M. A. *Polymer Chemistry* **2015**, *6* (19), 3641-3651.
- [95]. Suenaga, J.; Sutherlin, D. M.; Stille, J. K. *Macromolecules* **1984**, *17* (12), 2913-2916.
- [96]. Akkapeddi, M. K. *Polymer* **1979**, *20* (10), 1215-1216.
- [97]. Shin, J.; Lee, Y.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2012**, *13* (11), 3833-3840.
- [98]. Matyjaszewski, K.; Davis, T. P., *Handbook of radical polymerization*. Wiley Online Library: 2002.
- [99]. Matyjaszewski, K.; Tsarevsky, N. V. *Nature chemistry* **2009**, *1* (4), 276-288.
- [100]. Dong, H.; Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40* (9), 2974-2977.
- [101]. Thomas, D. B.; Sumerlin, B. S.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2003**, *36* (5), 1436-1439.
- [102]. Keddie, D. J. *Chemical Society Reviews* **2014**, *43* (2), 496-505.

- [103]. Matyjaszewski, K. *Science* **2011**, 333 (6046), 1104-1105.
- [104]. Mosnáček, J.; Yoon, J. A.; Juhari, A.; Koynov, K.; Matyjaszewski, K. *Polymer* **2009**, 50 (9), 2087-2094.
- [105]. Yi, Y.; Fan, X.; Wan, X.; Li, L.; Zhao, N.; Chen, X.; Xu, J.; Zhou, Q.-F. *Macromolecules* **2004**, 37 (20), 7610-7618.
- [106]. Liu, X.; Zhao, R.-Y.; Zhao, T.-P.; Liu, C.-Y.; Yang, S.; Chen, E.-Q. *RSC Advances* **2014**, 4 (35), 18431-18441.
- [107]. Braunecker, W. A.; Matyjaszewski, K. *Progress in Polymer Science* **2007**, 32 (1), 93-146.
- [108]. Butté, A.; Storti, G.; Morbidelli, M. *Macromolecules* **2001**, 34 (17), 5885-5896.
- [109]. Delaittre, G.; Charleux, B. *Macromolecules* **2008**, 41 (7), 2361-2367.
- [110]. Luo, Y.; Wang, X.; Zhu, Y.; Li, B.-G.; Zhu, S. *Macromolecules* **2010**, 43 (18), 7472-7481.
- [111]. Zhan, X.; He, R.; Zhang, Q.; Chen, F. *RSC Advances* **2014**, 4 (93), 51201-51207.
- [112]. Wang, S.; Vajjala Kesava, S.; Gomez, E. D.; Robertson, M. L. *Macromolecules* **2013**, 46 (18), 7202-7212.
- [113]. Hayashi, M.; Matsushima, S.; Noro, A.; Matsushita, Y. *Macromolecules* **2015**, 48 (2), 421-431.
- [114]. Vasile, C., *Handbook of polyolefins*. CRC Press: 2000.
- [115]. Natta, G. *Journal of polymer science* **1959**, 34 (127), 531-549.

- [116]. Harney, M. B.; Zhang, Y.; Sita, L. R. *Angewandte Chemie International Edition* **2006**, *45* (15), 2400-2404.
- [117]. Hotta, A.; Cochran, E.; Ruokolainen, J.; Khanna, V.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y.-W.; Shimizu, F.; Cherian, A. E.; Hustad, P. D. *Proceedings of the National Academy of Sciences* **2006**, *103* (42), 15327-15332.
- [118]. Crawford, K. E.; Sita, L. R. *ACS Macro Letters* **2015**, *4*, 921-925.
- [119]. Hadjichristidis, N. *Journal of Polymer Science Part A: Polymer Chemistry* **1999**, *37* (7), 857-871.
- [120]. Khanna, K.; Varshney, S.; Kakkar, A. *Polymer Chemistry* **2010**, *1* (8), 1171-1185.
- [121]. Bi, L.-K.; Fetters, L. J. *Macromolecules* **1976**, *9* (5), 732-742.
- [122]. Bi, L.-K.; Fetters, L. *Macromolecules* **1975**, *8* (1), 90-92.
- [123]. Lai, C.; Russel, W. B.; Register, R. A.; Marchand, G. R.; Adamson, D. H. *Macromolecules* **2000**, *33* (9), 3461-3466.
- [124]. Milner, S. T. *Macromolecules* **1994**, *27* (8), 2333-2335.
- [125]. Vavasour, J.; Whitmore, M. *Macromolecules* **1993**, *26* (25), 7070-7075.
- [126]. Lynd, N. A.; Oyerokun, F. T.; O'Donoghue, D. L.; Handlin Jr, D. L.; Fredrickson, G. H. *Macromolecules* **2010**, *43* (7), 3479-3486.
- [127]. Bates, F. S.; Fredrickson, G. H. *Annual Review of Physical Chemistry* **1990**, *41* (1), 525-557.

- [128]. Shi, W.; Lynd, N. A.; Montarnal, D.; Luo, Y.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Hexemer, A. *Macromolecules* **2014**, *47* (6), 2037-2043.
- [129]. Shi, W.; Hamilton, A. L.; Delaney, K. T.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Lynd, N. A.; Demassieux, Q.; Creton, C. *Macromolecules* **2015**, *48* (15), 5378-5384.
- [130]. Shi, W.; Hamilton, A. L.; Delaney, K.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Lynd, N. A. *Journal of the American Chemical Society* **2015**.
- [131]. Matmour, R.; Gnanou, Y. *Progress in Polymer Science* **2013**, *38* (1), 30-62.
- [132]. Jacob, S.; Kennedy, J. P. *Polymer Bulletin* **1998**, *41* (2), 167-174.
- [133]. Keszler, B.; Fenyvesi, G.; Kennedy, J. *Journal of Polymer Science Part A: Polymer Chemistry* **2000**, *38* (4), 706-714.
- [134]. Shim, J. S.; Asthana, S.; Omura, N.; Kennedy, J. P. *Journal of Polymer Science Part A: Polymer Chemistry* **1998**, *36* (17), 2997-3012.
- [135]. Shim, J. S.; Kennedy, J. P. *Journal of Polymer Science Part A: Polymer Chemistry* **1999**, *37* (6), 815-824.
- [136]. Shim, J. S.; Kennedy, J. P. *Journal of Polymer Science Part A: Polymer Chemistry* **2000**, *38* (2), 279-290.
- [137]. Dufour, B.; Koynov, K.; Pakula, T.; Matyjaszewski, K. *Macromolecular Chemistry and Physics* **2008**, *209* (16), 1686-1693.
- [138]. Dufour, B.; Tang, C.; Koynov, K.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Macromolecules* **2008**, *41* (7), 2451-2458.

- [139]. Pakula, T.; Koynov, K.; Boerner, H.; Huang, J.; Lee, H.-i.; Pietrasik, J.; Sumerlin, B.; Matyjaszewski, K. *Polymer* **2011**, *52* (12), 2576-2583.
- [140]. Juhari, A.; Mosnáček, J.; Yoon, J. A.; Nese, A.; Koynov, K.; Kowalewski, T.; Matyjaszewski, K. *Polymer* **2010**, *51* (21), 4806-4813.
- [141]. Feng, C.; Li, Y.; Yang, D.; Hu, J.; Zhang, X.; Huang, X. *Chemical Society Reviews* **2011**, *40* (3), 1282-1295.
- [142]. Uhrig, D.; Mays, J. *Polymer Chemistry* **2011**, *2* (1), 69-76.
- [143]. Ito, S.; Goseki, R.; Ishizone, T.; Hirao, A. *Polymer Chemistry* **2014**, *5* (19), 5523-5534.
- [144]. Uhrig, D.; Schlegel, R.; Weidisch, R.; Mays, J. *European Polymer Journal* **2011**, *47* (4), 560-568.
- [145]. Iatrou, H.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1998**, *31* (19), 6697-6701.
- [146]. Uhrig, D.; Mays, J. W. *Macromolecules* **2002**, *35* (19), 7182-7190.
- [147]. Beyer, F. L.; Gido, S. P.; Büschl, C.; Iatrou, H.; Uhrig, D.; Mays, J. W.; Chang, M. Y.; Garetz, B. A.; Balsara, N. P.; Tan, N. B. *Macromolecules* **2000**, *33* (6), 2039-2048.
- [148]. Duan, Y.; Thunga, M.; Schlegel, R.; Schneider, K.; Rettler, E.; Weidisch, R.; Siesler, H. W.; Stamm, M.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **2009**, *42* (12), 4155-4164.

- [149]. Weidisch, R.; Gido, S.; Uhrig, D.; Iatrou, H.; Mays, J.; Hadjichristidis, N. *Macromolecules* **2001**, *34* (18), 6333-6337.
- [150]. Staudinger, U.; Weidisch, R.; Zhu, Y.; Gido, S.; Uhrig, D.; Mays, J.; Iatrou, H.; Hadjichristidis, N. In *Mechanical properties and hysteresis behaviour of multigraft copolymers*, Macromolecular symposia, Wiley Online Library: 2006; pp 42-50.
- [151]. Schlegel, R.; Wilkin, D.; Duan, Y.; Weidisch, R.; Heinrich, G.; Uhrig, D.; Mays, J.; Iatrou, H.; Hadjichristidis, N. *Polymer* **2009**, *50* (26), 6297-6304.
- [152]. Goodwin, A. B.; Wang, W.; Kang, N.-G.; Wang, Y.; Hong, K.; Mays, J. W. *Industrial & Engineering Chemistry Research* **2015**.
- [153]. Wang, W.; Wang, W.; Lu, X.; Bobade, S.; Chen, J.; Kang, N.-G.; Zhang, Q.; Mays, J. *Macromolecules* **2014**, *47* (21), 7284-7295.
- [154]. Wang, W.; Wang, W.; Li, H.; Lu, X.; Chen, J.; Kang, N.-G.; Zhang, Q.; Mays, J. *Industrial & Engineering Chemistry Research* **2015**, *54* (4), 1292-1300.
- [155]. Li, H.; Wang, W.; Li, C.; Tan, J.; Yin, D.; Zhang, H.; Zhang, B.; Yin, C.; Zhang, Q. *Journal of colloid and interface science* **2015**, *453*, 226-236.
- [156]. Li, H.; Wang, W.; Tan, J.; Li, C.; Zhang, Q. *RSC Advances* **2015**, *5* (56), 45459-45466.
- [157]. Lichtenhan, J. D. *Comments on Inorganic Chemistry* **1995**, *17* (2), 115-130.
- [158]. Zheng, L.; Hong, S.; Cardoen, G.; Burgaz, E.; Gido, S. P.; Coughlin, E. B. *Macromolecules* **2004**, *37* (23), 8606-8611.

- [159]. Seurer, B.; Coughlin, E. B. *Macromolecular Chemistry and Physics* **2008**, *209* (12), 1198-1209.
- [160]. Schneider, Y.; Lynd, N. A.; Kramer, E. J.; Bazan, G. C. *Macromolecules* **2009**, *42* (22), 8763-8768.
- [161]. Coffin, R. C.; Schneider, Y.; Kramer, E. J.; Bazan, G. C. *Journal of the American Chemical Society* **2010**, *132* (39), 13869-13878.
- [162]. Jiang, F.; Wang, Z.; Qiao, Y.; Wang, Z.; Tang, C. *Macromolecules* **2013**, *46* (12), 4772-4780.
- [163]. Wang, Z.; Zhang, Y.; Jiang, F.; Fang, H.; Wang, Z. *Polymer Chemistry* **2014**, *5* (10), 3379-3388.
- [164]. Liu, Y.; Yao, K.; Chen, X.; Wang, J.; Wang, Z.; Ploehn, H. J.; Wang, C.; Chu, F.; Tang, C. *Polymer Chemistry* **2014**, *5* (9), 3170-3181.
- [165]. Wang, Z.; Jiang, F.; Zhang, Y.; You, Y.; Wang, Z.; Guan, Z. *ACS nano* **2014**, *9* (1), 271-278.
- [166]. Jiang, F.; Zhang, Y.; Fang, C.; Wang, Z.; Wang, Z. *RSC Advances* **2014**, *4* (104), 60079-60085.
- [167]. Jiang, F.; Zhang, Y.; Wang, Z.; Fang, H.; Ding, Y.; Xu, H.; Wang, Z. *Industrial & Engineering Chemistry Research* **2014**, *53* (52), 20154-20167.
- [168]. Jiang, F.; Zhang, Y.; Wang, Z.; Wang, W.; Xu, Z.; Wang, Z. *ACS applied materials & interfaces* **2015**.

Chapter 2: Scope of the Dissertation

2.1 Research Motivation:

After Milkovich and Holden first patented SIS triblock copolymer type TPEs in 1965¹, for almost 50 years, one of the major research goals in the field of anionic polymerization for industrial application has been to produce high temperature thermoplastic elastomers that meet the following requirements:

1). The polymer needs to be synthesized in hydrocarbon solvent at mild temperature, since most of the anionic polymerization capability in industry is designed for synthesis of PS-PI-PS triblock copolymer type thermoplastic elastomers under inert atmosphere in cyclohexane at around 60 °C. TPEs based on methyl methacrylate derivatives showed higher upper service temperature; however, polymerization in THF at -78 °C would not be a favorable choice for large-scale production.^{2,3} Another reason to avoid using THF as the solvent is that polymerizing isoprene or butadiene in THF increases the presence of the 1,2-microstructure, which compromises the elasticity.

2). For high temperature applications, the upper service temperature of the thermoplastic elastomers needs to be higher than 100 °C. One potential application of high temperature TPEs is to replace or reduce the amount of carbon black in tire compounding as a rigid filler. Since polymer weigh less than carbon black, reducing the amount of carbon black in tire would produce tires with lower weight, thus better fuel economy. However, this application received limited success with SIS TPEs due to the low glass transition temperature of PS.

3). Building blocks in the triblock copolymers need to microphase separate in order to form an efficient physical crosslink structure that enhances the tensile properties. Thus, exploring new building blocks with above mentioned requirements to prepare thermoplastic elastomers with high upper service temperature is of great interest in the anionic polymerization community.

Benzofulvene is a rigid conjugated diene monomer recently discovered to undergo living anionic polymerization in both the hydrocarbon solvent benzene at room temperature and the polar solvent THF at -78°C and produce polymers with T_g above 145°C .^{4,5} (**Figure 2.1**) This high temperature polymer with living anionic polymerization ability in hydrocarbon solvent at room temperature triggered our attention to incorporate PBF as a rigid block for TPE applications, since most of the reactors for anionic polymerization in pilot plants are designed for mild temperature polymerization in hydrocarbon solvents. Thus, the first motivation in this dissertation is to *evaluate the possibility of preparing ABA triblock copolymers with polybenzofulvene as the glassy end blocks and polyisoprene as the elastic middle block for high temperature thermoplastic elastomer applications.*

Well-defined multi-grafted copolymers PI-g-(PS)_n (n=1,2,3) with polystyrene as the glassy side chain and polyisoprene as the elastic backbone, indeed, showed great mechanical properties competitive with or greater than Kraton products. Considering the fact that preparing these materials required complicated titration anionic polymerization techniques and time consuming solvent/non-solvent fractionation,^{6,7} the

second motivation is to *develop a cost effective strategy to prepare graft copolymers for thermoplastic elastic application.*

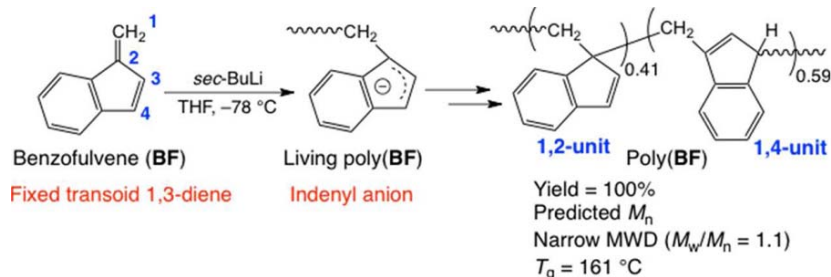


Figure 2.1: Anionic polymerization of benzofulvene⁴

2.2 Outline:

As **Chapter 1** summarized recent advances in the field of thermoplastic elastomers by using synthetic polymers, **Chapter 2** introduces the scope of the dissertation, and the rest of this thesis is arranged as follows:

Chapter 3 gives the overview of most experimental techniques with high vacuum lines used in this dissertation.

Chapter 4 describes the work of developing high temperature thermoplastic elastomers based on polybenzofulvene as the hard segment.

Chapter 5 describes further investigations into the effects of partial and complete hydrogenation on the properties of polybenzofulvene based TPEs.

Chapter 6 describes an economically viable method to prepare thermoplastic elastomers combining anionic polymerization and emulsion polymerization.

Chapter 7 concludes this thesis and provides future perspectives.

References:

- [1]. Geoffrey, H.; Ralph, M., Block polymers of monovinyl aromatic hydrocarbons and conjugated dienes. U.S. Patent No. 3,265,765: **1966**.
- [2]. Yu, J. M.; Dubois, P.; Jérôme, R. *Macromolecules* **1996**, 29 (26), 8362-8370.
- [3]. Yu, J. M.; Dubois, P.; Jérôme, R. *Macromolecules* **1996**, 29 (23), 7316-7322.
- [4]. Kosaka, Y.; Kitazawa, K.; Inomata, S.; Ishizone, T. *ACS Macro Letters* **2013**, 2 (2), 164-167.
- [5]. Kosaka, Y.; Kawauchi, S.; Goseki, R.; Ishizone, T. *Macromolecules* **2015**, 48 (13), 4421-4430.
- [6]. Iatrou, H.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1998**, 31 (19), 6697-6701.
- [7]. Uhrig, D.; Mays, J. W. *Macromolecules* **2002**, 35 (19), 7182-7190.